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*Studies on Explosion Reaction of Ethylene Mixed with Oxygen or Air. II. On the Explosion Peninsula**

By Masao SUGA

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(Received September 22, 1958)

In a previous paper[1], it has been shown that the explosion boundaries of ethylene mixed with oxygen and with air was determined by the "admission method" i. e., by sudden introduction of the premixed gases into a heated and previously evacuated vessel. Also, it has been noticed that the explosion, like that of the other combustible gases[2,3], occurred in a certain region of the pressure, temperature and composition of mixed gases. In this case, there are the first (the lower), the second (the upper) and the third (the thermal) limit in the definite composition and temperature range. The explosion peninsula lies in the range bounded by the first and the second pressure limit of explosion within which pale blue ignitions occurred. On the other hand, the explosion occurred normally with a blue flame which rapidly built up into a bright flash filling the reaction vessel and accompanied by a pulse in pressure. Also, it was apparent that the induction period of the explosion, the color of flame and the propagation velocity of flame were different in the two cases described.

Now the experiment has been made between 550°C and 700°C for mainly 20% ethylene with oxygen in order to observe in detail explosion phenomena in the explosion peninsula and to compare this with normal thermal explosion. The effects of nitrogen and vessel diameter on the explosion limit were studied. They will be briefly discussed.

Experimental

Materials. — The ethylene employed in this experiment was prepared by the dehydration of absolute ethanol and purified by the method described in the previous paper. The oxygen employed was obtained from a commercial cylinder (purity: 99.4%). The oxygen and the air were employed after being purified through a train consisting of two bottles containing a concentrated aqueous solution of sodium hydroxide and concentrated sulfuric acid. Before use, the gases were dried with phosphorus pentoxide.

Apparatus and Procedure. — The apparatus used and the procedure adopted were of the types described in the previous paper. This consisted of an electrically heated reaction vessel into which a gas mixture could be admitted from a separate mixing vessel. Subsequent explosion of the mixture could be observed visually through a small window of mica in the dark room, and a blue filter of 1 mm. thickness whose transmission curve** is shown in Fig. 1 was used to eliminate the red glow of the furnace so that an ignition could be detected. Cylindrical reaction vessels of quartz 15 cm. long and 3 cm. in standard diameter, were used, but the diameter was varied to 4 cm., 2 cm. or 1 cm. as required. The apparatus was evacuated down to 10^{-4}~10^{-5} mmHg (tested by Gaisler tube) with rotary and "Hücksman's diffusion" pump.

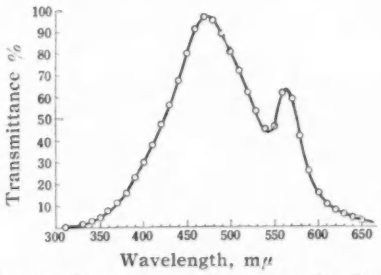

Fig. 1. The transmission curve of a filter.

Results and Consideration

The Explosion Limit.—Isochors for the explosion limits of 20% ethylene with oxygen and of 5% ethylene with air are shown respectively in Fig. 2 and Fig. 3. The evidence of an explosion was judged by observing the appearance of ignition, and usually the observation was continued for twenty minutes in the dark room.

* A part of this investigation was reported at the Annual Meeting of the Chûgoku-Shikoku Branch of the Chemical Society of Japan in Niihama, October 19, 1956.

1) M. Suga, This Bulletin, **31**, 515 (1958).

2) B. Lewis and N. von Elbe, "Combustion, Flames and Explosions of Gases", Academic Press, New York (1951), p. 29.

3) K. J. Laidler, "Chemical Kinetics", McGraw-Hill Book Co., Inc., New York (1950), p. 319.

** It was measured with a HITACHI Model EPB-U photo-electric spectrophotometer.

The results of observation were classified as follows:

(1) After the lapse of various induction periods (usually less than 10 sec.), luminous blue flames were observed.

(2) After the lapse of the relatively long induction periods (6 sec.~20 min.), pale blue flames were observed in the dark room.

(3) No flame could be found even in the dark room.

Case 1, 2 and 3 are indicated respectively by ◎, ○ and × in Figs. 2 and 3. Also ⊕ in Fig. 2 indicates the case of the luminous flame propagating into the storage bulb owing to the shorter induction period than 0.8 sec. and the large propagation velocity of flames.

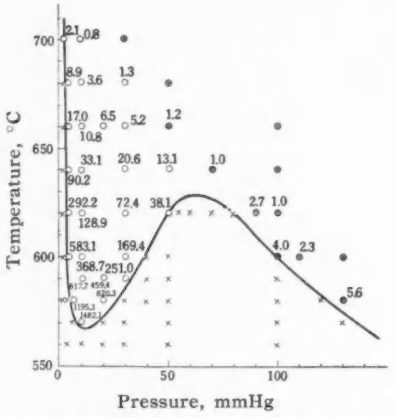

Fig. 2. Explosion limit of 20% ethylene with oxygen. (Induction periods in seconds are indicated by numbers beside observation points.)

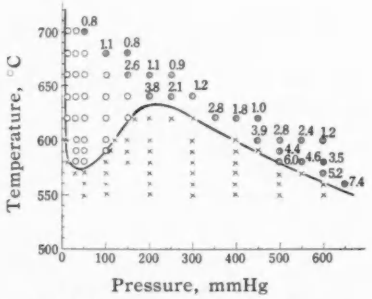

Fig. 3. Explosion limit of 5% ethylene with air. (Induction periods in seconds are indicated by numbers beside observation points and the results of longer induction period will be indicated in Fig. 6).

It is evident from the isochors that the first, the second and the third pressure limit of explosion exist in the explosion limit of ethylene-oxygen and -air mixtures. The first pressure limit of explosion does not seem to depend to a great extent on temperature, but the observation was more or less obscure because of the low admission pressure. The boundary of the first and the second pressure limit of explosion, i. e., the tip of the explosion peninsula, was determined from the results of observation for thirty minutes. The second pressure limit of explosion increases abruptly with increasing temperature, and, on the other hand, the third pressure limit of explosion decreases with increasing temperature.

Fig. 4 shows the isochors for the explosion limits of ethylene-oxygen mixtures. In this case, the explosion peninsula results in various shapes according to the composition of gas mixtures. That is to say, the composition of gas mixture affects the explosion limit considerably, and particularly it was noticed that the explosion peninsula disappears at over 25% ethylene with oxygen.

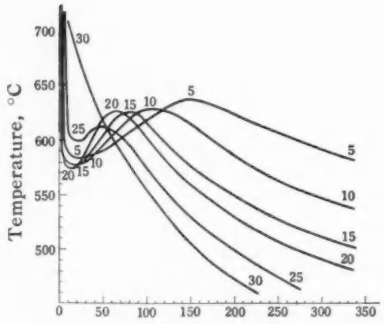

Fig. 4. Isochors for explosion limit of ethylene-oxygen mixtures. curve 5=5%, 10=10%, 15=15%, 20=20%, 30=30% ethylene.

The Effect of Nitrogen in the Air.—As shown in the previous paper, the third pressure limits of explosion for ethylene with oxygen and with air were equivalent to each other in spite of the differences of the propagation velocity of flame, the induction period, etc., so far as the partial pressure of nitrogen was neglected. Also, in order to elucidate the effect of nitrogen, an isochor for explosion limit of 20% ethylene with oxygen is shown and this is plotted with the corresponding points

of the results for explosion limit of 5% ethylene with air, by calculation, subtracting the partial pressure of nitrogen.

This plot is shown by the broken line in Fig. 5. It is concluded that the first and the third pressure limit of explosion are slightly lower, and, the on other hand, the second pressure limit of explosion considerably lower, than the corresponding full line. In other words, nitrogen affects the second pressure limit of explosion, but does not affect the first and the third pressure limit of explosion.

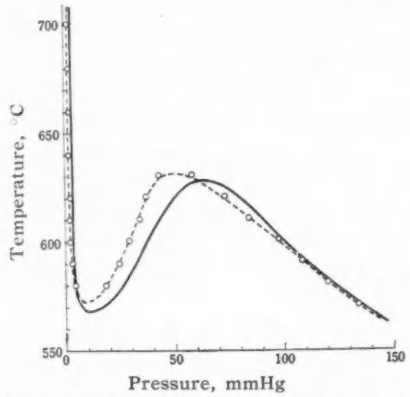

Fig. 5. Effect of nitrogen on isochor for explosion limit of 20% ethylene with oxygen. (Broken line represents the data calculated from the limit of 5% ethylene with air, Fig. 3.)

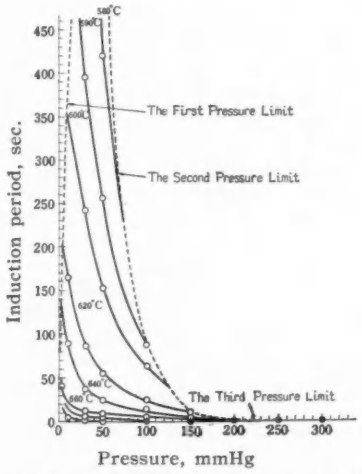

Fig. 6. Relationship between explosion limit pressure and induction period at definite temperatures for 5% ethylene with air.

The Explosion Limit and Induction Period. — The results of the experiment with regard to the induction period are shown by numbers beside the observation points in Figs. 2 and 3. The induction period was measured by a stopwatch. But in cases where the admission time required more than 0.6 sec., the induction period could not always be measured by a stopwatch with high accuracy. Fortunately, induction period is fairly long in the region

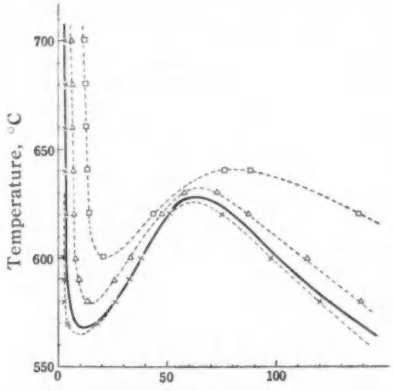

Fig. 7. Effect of reaction vessel diameter on isochor for explosion limit of 20% ethylene with oxygen. Diameter: Full line, 3 cm.; □, 1 cm.; △, 2 cm.; ×, 4 cm.

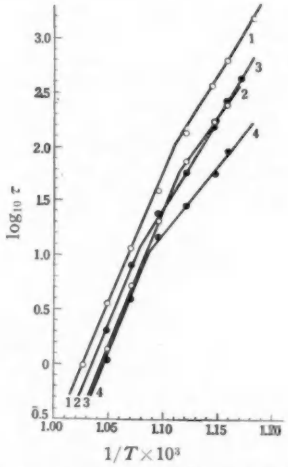

Fig. 8. $\log_{10}\tau$ against $1/T$ curves for the explosion of 20% ethylene with oxygen and 5% ethylene with air.
○; 20% C_2H_4 with O_2, curve 1=10, 2=30 mmHg admission pressure, ●; 5% C_2H_4 with air, curve 3=50, 4=10 mmHg admission pressure.

of the explosion peninsula and is reproducible so far as precautions are taken in accord with standard procedure[1]. Fig. 6 shows the relationship between explosion limit pressure and induction period at various different temperatures for 5% ethylene with air.

The Effect of Reaction Vessel. — For reaction vessels, quartz cylinders of 3 cm. in diameter and 15 cm. in length were usually employed. Quartz cylinders of 4, 2 and 1 cm. in diameter of the same length were also employed in order to compare the effects of the diameter of reaction vessels. The results are indicated in Fig. 7. The decrease of the vessel diameter increaed the first and the third pressure limit, and, on the other hand, lowered the second pressure limit of explosion; i. e., the decrease of the vessel diameter serves invariably to retard the explosion. It is noticed that the second pressure limit of explosion suffers the effect of the surface of the vessel only slightly, and in consequence, the explosion peninsula tends to disappear when the specific surface of the vessel is increased.

The Activation Energy of the Reaction. —In Fig. 8 is shown the relationship between the absolute temperature T and the induction period τ in relation to the results of Fig. 2 and Fig. 6. Every curve bends at the neighborhood of ca. 620°C, but is essentially linear and holds the relationship $\log_{10}\tau = A/T + B$. On the other hand, while this result has no direct relationship with the meaning of kinetics and the adaptability of the former's formula to the latter is questionable, nevertheless the gradient of these lines, A, is thought to be equal to $E/2.303\times R$[4,5]. Thus, values for E, the apparent activation energy, may be as in Table I.

TABLE I. ACTIVATION ENERGIES ESTIMATED FROM THE INDUCTION PERIOD

Curve	A	$E=2.303\times1.987\times A$ (kcal./mol.)
1	15.03	68.77
	22.35	102.27
2	13.77	63.01
	24.30	111.97
3	15.27	69.88
	23.73	108.59
4	13.53	61.91
	23.73	108.59

4) B. P. Mullins, "Spontaneous Ignition of Liquid Fuels", Butterworths Sci. Pub., London (1955).
5) N. Semenoff, *Z. Physik*, **48**, 57 (1928).

Summary

In the previous paper, the explosion limit of ethylene mixed with oxygen and with air by the "admission method" was presented. It was pointed out that the explosion peninsula lies in the region between the first and the second pressure limit of explosion. The results of observation in this region differ from those in thermal explosion.

In the present experiment, the following results have been obtained.

(1) The explosion peninsulas of ethylene-oxygen and ethylene-air mixtures lie approximately in the range of the same temperature and pressure limits as that of carbon monoxide-oxygen mixture[6].

(2) If ethylene concentration exceeds ca. 25% ethylene with oxygen, the explosion peninsula disappears.

(3) The induction period of explosion in the explosion peninsula is relatively longer than those of other thermal explosions.

(4) In the explosion within the explosion peninsula, the apparent activation energy estimated in accordance with Semenoff's theory is of abnormally high value. Merely from these facts, it is difficult to determine the explosion mechanism of ethylene-oxygen mixture, but it is possible for one to assume that the explosion within the explosion peninsula has a different mechanism from other thermal explosions.

If one refers to the studies of Neumann and Serbinoff[7], Norrish and Food[8], and Lewis[2] on the explosion of methane-oxygen mixture, he will find that the explosion peninsula which is observed in the explosion limit of ethylene-oxygen or -air mixtures is not always related to the nature of ethylene itself. In other words, ethylene-oxygen mixture is decomposed into carbon monoxide first in the definite range of temperature and pressure. Furthermore, it is considered that carbon monoxide which is produced and accumulated in slow oxidation of ethylene, i. e., slow reaction, is ignited in the definite condition. Thus, if ethylene concentration is greater than the stoichiometric value crresponding to $C_2H_4+3O_2=2CO+2H_2O$, the oxygen which is required to oxidate this carbon monoxide is insufficient, and therefore the

6) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **50**, 37 (1954).
7) M. Neumann and A. Serbinoff, *Phys. Z. Sowjet*, **1**, 536 (1932).
8) R. G. W. Norrish and S. G. Food, *Proc. Roy. Soc.*, **A 157**, 503 (1936).

explosion peninsula disappears. The conclusion is a little too speculative, but it is considered that the explosion peninsula of ethylene-oxygen or -air mixtures originates in the oxidation of carbon monoxide which is accumulated in slow reaction.

The author wishes to express his gratitude to the late Professor R. Kiyama and Dr. J. Ôsugi of the Kyôto University and Professor T. Kôzu for their kind advice and encouragement throughout this work. He is also grateful to Mr. T. Ogura and Mr. Y. Takasuga for their assistance in the observations as a part of the present experiment.

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Dissociation Constants of Some Carboxylic Acids in Mixed Aqueous Solvents

By Motoo YASUDA

(Received October 9, 1958)

The dissociation constants of carboxylic acids were determined by various authors in mixed solvents, such as water-methanol, water-ethanol and water-dioxane mixtures and the relationship between the dissociation constants of the acids and the dielectric constants of the mixed solvents was discussed. As the dissociation of an acid is influenced by the dielectric constant of the solvent, it may be reasonable to suppose that an acid has almost the same acidity, i. e., almost the same dissociation constant in mixed solvents having the same dielectric constant. However, both Speakman[1] and Dondon[2] observed that aqueous dioxane acted as if it had a higher effective dielectric constant than aqueous alcohol of the same bulk dielectric constant. In other words, the values of dissociation constants of several acids in aqueous dioxane were reported to be higher than those determined in aqueous alcohol with the same dielectric constant. The present paper deals with the problem whether a carboxylic acid has really different acidity in various mixed solvents having the same dielectric constant.

Calculation of the Dissociation Constants. — The dissociation of a carboxylic acid in mixed solvents is an equilibrium reaction of the type

$$HA + S \rightleftarrows SH^+ + A^- \qquad (1)$$

where HA is a monobasic acid and S is one of the components of the mixed solvent. Since water has an exceptionally high proton affinity, Eq. 1 may be written as Eq. 2, if the mixed solvent contains a sufficient quantity of water and the concentration of the acid is small.

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \qquad (2)$$

The equilibrium constant of this dissociation, or the dissociation constant of an acid in aqueous mixed solvents should be given by Eq. 3:

$$K = [A^-]\,[H_3O^+] / [HA]\,[H_2O] \qquad (3)$$

where square brackets indicate activity. On the other hand, the strength of an acid in water is usually expressed in terms of the constant K_a, instead of K defined by Eq. 3,

$$K_a = [A^-]\,[H^+] / [HA] \qquad (4)$$

In aqueous solution K_a may be used, for $[H_2O]$ is nearly constant. But this is not true in mixed solvents containing a limited amount of water. Due consideration should be paid to the fact that the activity of water in mixed solvents changes with the molar fraction of organic solvents. Therefore, the constant K defined by Eq. 3 should be used for the estimation of the dissociation of an acid in mixed solvents, in place of K_a defined by Eq. 4.

Furthermore, K_a has a different numerical value in accordance with the unit of concentration used in calculation, whereas

1) J. C. Speakman, *J. Chem. Soc.*, **1943**, 270.
2) M. -L. Dondon, *J. chim. phys.*, **54**, 290, 304 (1957).

K does not depend on the unit of concentration. The present author calculated the values of K from the values of K_a reported by previous workers. But, as the activity of water in mixed solvents containing electrolytes is not known, it was replaced by the concentration of water.

Results and Discussion

1) Benzoic, Adipic and Succinic Acids.— Speakman determined the dissociation constant K_a defined by Eq. 4 of some carboxylic acids in aqueous alcohols and dioxane by using a glass electrode in conjunction with a cell involving liquid-liquid potentials. Some of his results are listed in Table I together with the dielectric constants ε reported by him. As seen in Table I, the values of $pK_a(=-\log K_a)$ in aqueous dioxane are lower than those of pK_a in aqueous alcohol having the same dielectric constant. The present author calculated the values of pK defined by Eq. 3 considering the change in the amount of water in mixed solvents. The values of the first and the second dissociation constant, pK_1 and pK_2, recalculated in this way are listed in Table II.

The values of pK are plotted against $1/\varepsilon$ in Fig. 1. It is seen that all points fall on a straight line. This means that an acid has nearly the same acidity in the medium having the same dielectric constant, at least in the range of the dielectric constant studied.

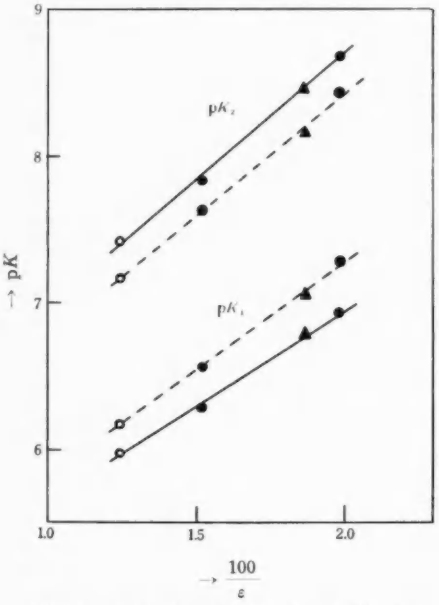

Fig. 1. Variation of pK values with the dielectric constant of the solution. Solid and broken lines indicate succinic and adipic acids, respectively. White and black circles and triangles show values in water, water-alcohol and water-dioxane mixtures, respectively.

TABLE I. VALUES OF pK_a AT 20°C REPORTED BY SPEAKMAN

Solvent % by wt.	ε	Adipic acid		Succinic acid		Benzoic acid
		pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}	pK_a
Water	80.4	4.43	5.42	4.22	5.67	4.24
25% Ethanol	65.7	4.93	6·00	4.65	6.19	4.83
50% Ethanol	50.4	5.83	6.98	5.48	7.24	5.87
30% Dioxane	53.3	5.45	6.55	5.19	6.84	5.35

TABLE II. RECALCULATED VALUES OF pK AT 20°C

Solvent % by wt.	Adipic acid		Succinic acid		Benzoic acid
	pK_1	pK_2	pK_1	pK_2	pK
Water	6.17	7.16	5.96	7.41	5.98
25% Ethanol	6.55	7.62	6.27	7.81	6.45
50% Ethanol	7.27	8.42	6.92	8.68	7.31
30% Dioxane	7.04	8.14	6.78	8.43	6.94

2) Succinic and Azelaic Acids. — In addition to the work of Speakman, Dondon reported recently the values of dissociation constants of several dibasic acids in water-methanol, water-ethanol and water-dioxane mixtures. A part of her results is shown in Fig. 2. She also reported that the dissociation of acids in aqueous dioxane is larger than in aqueous alcohols with the same dielectric constant. The values of pK_a determined by her in water-dioxane and in water-alcohol mixtures fall on two separate curves when they are plotted against $1/\varepsilon$. The range of the solvent composition studied for succinic acid by Dondon is wider than that by Speakman. She used the molarity basis for the calculation, but Speakman used the molality basis.

Now Dondon's values of pK_a are recalculated to give those of pK_1 and pK_2, which are listed in Table III. The values of density of the aqueous mixed solvents used for calculation were taken from Landolt-Börnstein's Tables[3] and the data

3) Landolt-Börnstein, "Physikalisch-Chemische Tabellen", Verlag J. Springer, Berlin, Hauptwerk (1923), p. 448 and Zweiter Ergänzungsband (1931), p. 287.

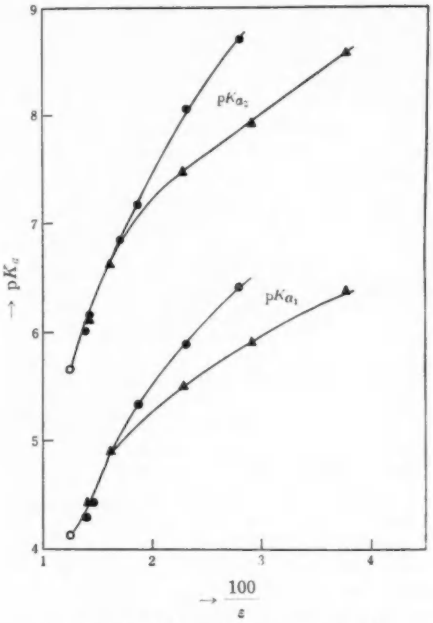

Fig. 2. Variation of pK_a values of succinic acid with the dielectric constant of the solution. White and black circles and triangles show values in water, water-alcohol and water-dioxane mixtures, respectively.

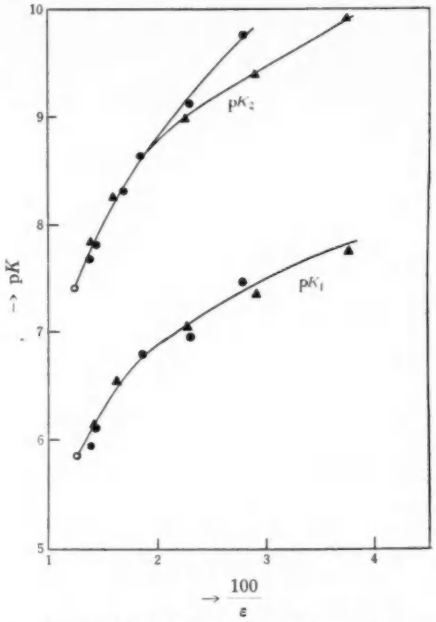

Fig. 3. Variation of pK values of succinic acid with the dielectric constant of the solution. White and black circles and triangles show values in water, water-alcohol and water-dioxane mixtures, respectively.

reported by Dunsmore and Speakman[4]. When the values of pK_1 and pK_2 are plotted against $1/\varepsilon$ (Fig. 3), all points of pK fall on a curve, except the points of pK_2 of succinic acid in the range of ε smaller than 40.

TABLE III. RECALCULATED VALUES OF pK_1 AND pK_2 AT 20°C

Solvent % by vol.	ε	Succinic acid		Azelaic acid	
		pK_1	pK_2	pK_1	pK_2
Water	80.4	5.88	7.41	6.29	7.24
20% Methanol	72.3	5.96	7.68	6.48	7.76
50% Methanol	59.0	6.46	8.31	6.96	8.31
80% Methanol	43.5	6.95	9.10	7.60	8.98
20% Ethanol	70.5	6.12	7.82	6.53	7.86
50% Ethanol	54.0	6.82	8.64	7.49	8.82
80% Ethanol	36.0	7.48	9.75	8.12	9.65
10% Dioxane	71.0	6.15	7.82	6.39	7.77
20% Dioxane	62.0	6.57	8.27	6.67	8.05
40% Dioxane	44.0	7.04	8.99	7.67	9.00
50% Dioxane	34.5	7.34	9.36	8.18	9.57
60% Dioxane	26.5	7.71	9.92	8.80	10.26

4) H. S. Dunsmore and J. C. Speakman, *Trans. Faraday Soc.*, **50**, 236 (1954).

For the irregularity of pK_2 of succinic acid, it is difficult to find the cause. One cause now suspected is the change of the distance between the secondly dissociating proton and the previously dissociated carboxyl group in different mixed solvents.

Although Dondon reported dissociation constants determined in 100% methanol, 100% ethanol and 80% dioxane, these data were not used in the calculation, for the dissociation of an acid in pure organic liquids is different from that shown by Eq. 2 and she reported that the data for 80% dioxane were least reliable.

3) Acetic Acid. — The dissociation constant of acetic acid in mixed aqueous solvents was determined by several authors[5-7]. The same situation as mentioned above was also found for acetic acid. The values of pK_a originally reported and those of pK recalculated for acetic acid are listed in Table IV and

5) T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

6) A. L. Bacarella, E. Grunwald and H. P. Marshall, *J. Org. Chem.*, **20**, 747 (1955).

7) H. S. Harned and G. L. Kazanjian, *J. Am. Chem. Soc.*, **58**, 1912 (1936).

these values of pK are plotted against $1/\varepsilon$ in Fig. 4. The dielectric constants, ε, of the mixed solvents were calculated by interpolation using the data of Gosting and Albright[8].

As shown in Tables II, III and IV, all the values of pK for acetic, benzoic, succinic, azelaic and adipic acids were calculated using the concentration of water instead of its activity. Nevertheless a carboxylic acid has almost the same dissociation constant in various mixed solvents having the same dielectric constant. The apparently greater acidity of a carboxylic acid in the water-dioxane mixture reported previously is due to the greater concentration of water in this mixture than in the water-alcohol mixture having the same dielectric constant.

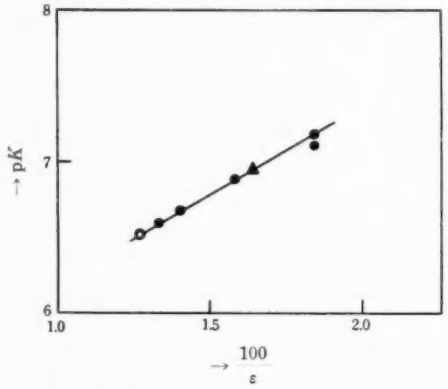

Fig. 4. Variation of pK values of acetic acid with the dielectric constant of the solution. White and black circles and triangle show values in water, water-alcohol and water-dioxane mixtures, respectively.

TABLE IV. THE DISSOCIATION CONSTANT OF ACETIC ACID AT 25°C

Solvent	ε	pK_a	pK
Water	78.5	4.76[3]	6.50
10% Methanol (by vol.)	75.0	4.88[3]	6.58
20% Methanol (by vol.)	71.3	5.02[3]	6.67
40% Methanol (by vol.)	63.2	5.34[3]	6.88
60% Methanol (by vol.)	54.4	5.74[3] 5.81[6]	7.10 7.17
20% Dioxane (by wt.)	60.8	5.29[7]	6.94

Summary

Several authors determined dissociation constants of acids such as benzoic, succinic and azelaic acids in mixed solvents and reported that the dissociation constants determined in aqueous dioxane were higher than those determined in aqueous alcohols having the same dielectric constants. However, if the variation of the amount of water in mixed solvents is taken into consideration in calculating the dissociation constant, an acid has almost the same dissociation constant in various mixed solvents with the same dielectric constant.

The author is greateful to Professor K. Yamasaki and Professor H. Kakihana, who read the manuscript and made helpful comments and criticism.

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8) P. S. Albright and L. J. Gosting, ibid., **68**, 1061 (1946).

Interaction Polarization of the Hydrogen Bonded Complexes

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A strong intermolecular interaction such as hydrogen bonding will be expected to give rise to some variation in the charge distribution of the interacting molecules[1]. Hence the dielectric measurement for the system containing hydrogen bonds will give some useful information about the intermolecular association through hydrogen bonding. Hammic, Norris and Sutton[2] investigated the polarization of molecular complexes from this point of view and pointed out[3] that it was not generally practicable to derive both the association constant and the dipole moment of a complex from polarization data alone. Few and Smith[4] also studied this problem, and proposed a method by which both values for a complex were obtained from the dielectric measurement alone. The association constant of a complex derived by them, however, was much lower than the value obtained by other methods such as infrared absorption spectroscopy. Although their analysis is correct, in principle, such a discrepancy may probably result from the difficulty in estimating polarization owing to the solvent effect within the accuracy of 0.1 cc. If an accurate correction for the solvent effect is possible, the method proposed by them will be applied extensively.

This report describes a somewhat different approach from those above mentioned to the interaction polarization of hydrogen bonded complexes such as benzyl alcohol-dioxane and phenol-dioxane in benzene.

Experimental

All materials used in this work were purified by the standard method[5], and dried carefully. The solvent used throughout this work was benzene which was a very "*good solvent*" compared with other non-polar solvents such as cyclohexane or carbon tetrachloride.

Molecular polarizations were determined by measuring dielectric constants ε, refractive indexes n and specific volumes v of the binary or the ternary solutions. The apparatus for the dielectric measurement is almost the same as that generally used; that is to say, the heterodyne beat method. A very stable oscillator is necessary in order to obtain high accuracy, so the circuits devised by Gouriet[6] are employed without any improvement. The beat frequency of both tank circuits was again coupled with a standard tuning fork by making use of the cathode-ray oscilloscope. The dielectric cell was made of nickel and has three coaxial cylindrical electrodes[7], the outer side of which are connected to the ground. The capacity of the cell is about 100 pF. The cell constant was determined by carefully purified and dried benzene. An oil bath was used as a thermostat to minimize the error due to stray capacity. The temperature was kept at 25 ± 0.05°C throughout this work. The refractive index of the solution was measured by a Pulfrich refractometer, and a sodium lamp was used as the light source. The density of the solution was determined by a Lipkin pycnometer.

The calculation of molecular polarization was performed according to Halvelstadt and Kumler's method. For the ternary systems, the amount of the proton acceptor, that is dioxane, was kept constant and the polarization was extrapolated to zero concentration with regard to the proton donor.

Results

The results of the measurements of ε, n^2 and v for the two ternary systems, i.e., benzyl alcohol-dioxane-benzene and phenol-dioxane-benzene, are summarized in Table I together with those for the corresponding binary systems, i.e., benzyl alcohol-benzene and phenol-benzene. Experimentally determined formulae relating ε, n^2 and v to w, respectively, are also included in Table I for each system, where w represents the weight fraction of the proton donor.

1) See the following reviews. C. A. Coulson, *Research*, **10**, 147 (1957); L. Keller, *Repts. Progr. in Phys.*, **15**, 1 (1952).
2) J. W. Smith, "Electric Dipole Moments", Butterworths Scientific Publications, London (1955).
3) J. R. Hulett, J. A. Pegg and L. E. Sutton, *J. Chem. Soc.*, **1955**, 3901.
4) A. V. Few and J. W. Smith, ibid., **1949**, 2781.
5) A. Weissberger, et al., "Organic Solvents", Interscience Publishers, New York (1955).
6) G. G. Gouriet, *Wireless Engineer.*, **72**, 105 (1950).
7) A. W. Weissberger, et al., "Physical Methods of Organic Chemistry III", Interscience Publishers, New York (1954), p. 2293.

TABLE I. DIELECTRIC CONSTANTS, REFRACTIVE INDEXES AND DENSITIES OF THE TERNARY AND THE BINARY SYSTEMS

$w\times10^2$	ε	n^2	v	
Benzyl alcohol-Dioxane-Benzene				
(The weight percentage of dioxane is 31.26)				
0	2.2593	2.1791	1.0895	
0.26	2.2689	2.1795	1.0893	$\varepsilon=2.2593+3.14w$
0.50	2.2766	2.1800	1.0887	$n^2=2.1791+0.167w$
1.49	2.3106	2.1816	1.0873	$v=1.0895-0.146w$
2.18	2.3353	2.1827	1.0863	
Benzyl alcohol-Benzene				
0	2.2725	2.2427	1.1446	
0.51	2.2878	2.2433	1.1434	$\varepsilon=2.2725+3.10w$
0.94	2.3011	2.2439	1.1429	$n^2=2.2427+0.109w$
2.28	2.3431	2.2453	1.1402	$v=1.1446-0.190w$
2.98	2.3666	2.2460	1.1390	
Phenol-Dioxane-Benzene				
(The weight percentage of dioxane is 41.05)				
0	2.2556	2.1578	1.0729	
0.50	2.2781	2.1591	1.0717	$\varepsilon=2.2556+4.26w$
0.99	2.2986	2.1603	1.0710	$n^2=2.1578+0.251w$
2.33	2.3554	2.1640	1.0688	$v=1.0729-0.160w$
3.69	2.4117	2.1671	1.0667	
Phenol-Benzene				
0	2.2725	2.2427	1.1446	
0.29	2.2813	2.2433	1.1439	$\varepsilon=2.2725+2.82w$
0.52	2.2866	2.2437	1.1434	$n^2=2.2427+0.15w$
0.77	2.2944	2.2441	1.1427	$v=1.1446-0.242w$
1.44	2.3131	2.2450	1.1411	

Polarization values calculated from these experimental data are shown in Table II, where p or P is the specific or the molecular polarization, and r or R the corresponding refraction. The values of dipole moment were evaluated on the assumption that $P_{E+A}=[R_D]$ or $P_{E+A}=1.05$ $[R_D]$ and shown in the same table as μ or μ'.

TABLE II. POLARIZATIONS AND DIPOLE MOMENTS OF THE HYDROGEN BONDED COMPLEXES AND THE FREE PROTON DONORS

	Benzyl alcohol -Dioxane	Benzyl alcohol	Phenol-Dioxane	Phenol
p	0.9039 cc.	0.8674	1.0264	0.8993
r	0.2074 cc.	0.3005	0.3009	0.2931
P	97.7 cc.	93.8	96.6	84.9
R_D	32.1 cc.	32.5	28.3	27.6
μ	1.79 D	1.73	1.84	1.67
μ'	1.76 D	1.70	1.82	1.65

Attention was called especially to the association among the proton donors. For example, when the dipole moment of benzyl alcohol was measured in cyclohexane, the value obtained was 1.55 D or so which was a little smaller than 1.70 D[8] of methanol measured in the vapor phase. This fact seems attributable probably to the association of benzyl alcohol in this solvent. On the other hand, we used benzene as a solvent for benzyl alcohol and could obtain almost the same dipole moment as that of methanol in the vapor phase. Infrared absorption spectroscopy showed that the bridged bands were not perceived at concentrations less than ca. 0.01 mol./l. in carbon tetrachloride. Although the dielectric measurements in such a dilute solution are desirable, the change in the dielectric constants within the range of concentrations where the bridged bands are not observed, is not detected by the present apparatus and technique. But it seems probable that the fraction of solutes capable of existing as free molecules without association is more or less altered from one solvent to another. Although we have not ascertained it, it seems appropriate to use benzene as the dispersing solvent to minimize the effect of association of solutes.

For the ternary systems a few remarks must be added. The dielectric constant of the mixed solvent composed of ca. 0.7 benzene and 0.3 dioxane in weight fraction is about 2.26 compared with 2.27 of bezene. Even such a small change in the dielectric constant of the medium may cause the change in polarization due to the solvent effect. Generally speaking, the following factors are considered to contribute to the solvent effect: (1) dielectric constant of the medium, (2) anisotropy of solvent molecules, (3) polarizability of solute molecule and (4) geometrical shape of the solute molecule. The change in polarization by the first factor was estimated as the order of magnitude of 0.1 cc.[9] Contributions of the other factors are difficult to estimate, but will probably lie within the limit of experimental errors. The experiemntal data for the ternary systems were, therefore, employed without any correction for the solvent effect. Molecular polarization obtained by the usual method of extrapolating to zero concentration contains, however, the contributions of both the free molecules and the molecular complexes. In order to divide the observed value into polarization of the free

8) A. A. Maryott and F. Bucklay, *N. B. S. Circular*, **537**, 13 (1953).
9) K. Shogenji, *J. Phys. Soc. Japan*, **12**, 166 (1958).

molecules and that of the molecular complexes, the following procedure was adopted.

Let us consider the equilibrium for the complex formation between molecules A and B. We assume the interaction between A and B to be one to one. The equilibrium constant of this system is

$$K=\frac{x}{(a-x)(b-x)}=\frac{1}{(a-x)(b/x-1)} \qquad (1)$$

where a and b are concentrations of molecular species A and B, respectively, in the initial state and x is that of the molecular complex. A is dioxane and B is benzyl alcohol or phenol in the present work. When b is reduced smaller, x also diminishes, and the ratio $f_x=x/b$, i.e., the fraction of the complex in the system approaches to a definite value,

$$\lim_{b\to 0} f_x=\lim_{b\to 0} x/b=aK/(aK+1) \qquad (2)$$

since x becomes negligible against a in the denominator of Eq. 1. The formation constants are reported to be about 5,000[10] and 9,400[11] for benzyl alcohol-dioxane and phenol-dioxane complexes, respectively, using mol./cc. as the unit of concentration. Hence f_x is calculated to be 0.942 for the former, and 0.976 for the latter. The contribution of the free proton donor to the observed polarization is, therefore, estimated as $93.8\times 0.058=5.4$ in the former, and $84.6\times 0.024=2.0$ in the latter. If the difference between the observed polarization and the above one is divided by the fraction of the complex, then the value for the true polarization of the complex is obtained as 97.9 cc. for benzyl alcohol-dioxane, and 96.9 cc. for phenol-dioxane. These values are almost the same as those without any correction. It can therefore be concluded that there is no need for this correction when the equilibrium constant is comparatively large and, moreover, the nonpolar proton acceptors exist in large quantities.

Discussion

Perturbation of the proton donor by the proton acceptor and vice versa will be relatively small since the energy of hydrogen bonding is generally about 5 kcal./mol. or so. Hence, the deformation of σ-orbitals or even that of lone pair orbitals not participating in the hydrogen bond but existing in its neighborhood, is completely out of the question in the present treatment as generally believed, whereas in the case of the polarizable π-orbitals their deformation is comparatively large even by a small perturbation. It seems probable therefore that the change in the distribution of π-electrons may be induced by the access of lone pair electrons of a proton acceptor within the range of van der Waals radius. Coulson and Sutton[12] already discussed the hyperpolarizability of benzene and pointed out the importance of this effect in the vicinity of an ion or a dipole. The system of benzyl alcohol-dioxane will not need consideration of the hyperpolarizability as already stated. Contrary to this, the system of phenol-dioxane is supposed to receive a comparatively large effect. It will, therefore, be necessary first to consider the polarizability of the π-electrons of phenol due to the lone pair field of the proton acceptor. To estimate this effect, we try at first to determine the simple molecular orbitals of phenol and those of dimethyl ether, the molecular size of which is presumed to be half as great as a dioxane molecule, and then to evaluate the induced polarization of the π-orbitals of phenol. Then a brief discussion on the delocalization due to hydrogen bonding will be given.

Molecular Orbitals of the π-Electrons of Phenol.—Molecular orbitals of π-electrons of phenol were determined by the use of Matsen's parameter[13]. All the notations used in this section are the same as those of Matsen's paper. According to the molecular symmetry the secular determinant of the seventh order was factored into one of the second and one of the fifth order. All the orbitals obtained by solving these secular determinats are shown in Table III. Orbitals belonging to the symmetry group B_1 are the same as those of benzene, whereas those of A_1 receive a modification as shown in this table. An energy and a moment of each molecular orbital are also tabulated. The calculated π-moment is 1.46 D and its direction is directed toward the benzene ring from the

10) N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951). Measurements were made at room temperature.

11) H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955). As the values reported were in the range between 9.4 and 9.8 in the unit of mol./l., the lower value of 9.4 was adopted here.

12) C. A. Coulson and L. E. Sutton, *Trans. Faraday Soc.*, **48**, 106 (1952).

13) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

TABLE III. COEFFICIENTS, ENERGIES AND MOMENTS OF THE π-ORBITALS OF PHENOL

B_1:	M.O.	energy	moment
	$\chi_2=\phi_2$	$\alpha+\beta$	10.632 a.u.
	$\chi_4=\phi_4$	$\alpha-\beta$	—

A_1: $\chi_i=c_{i1}\varphi_1+c_{i3}\varphi_3+c_{i5}\varphi_5+c_{i6}\varphi_6+c_{i7}\varphi_7$

c_{11}	0.601	c_{13}	0.283	c_{15}	0.107
		c_{16}	0.066	c_{17}	0.736
c_{71}	0.786	c_{73}	−0.370	c_{75}	−0.101
		c_{76}	−0.052	c_{77}	−0.481
c_{31}	0.136	c_{33}	0.880	c_{35}	−0.143
		c_{36}	−0.143	c_{37}	−0.427
c_{51}	0.026	c_{53}	0.055	c_{55}	0.973
		c_{56}	−0.093	c_{57}	−0.202
c_{61}	0.012	c_{63}	0.022	c_{65}	0.066
		c_{66}	0.989	c_{67}	−0.121

M.O.	energy	moment
χ_1	$\alpha+2.494\beta$	3.379
χ_7	$\alpha+1.749\beta$	10.090
χ_3	$\alpha+0.722\beta$	8.369
χ_5	$\alpha-1.116\beta$	—
χ_6	$\alpha-2.050\beta$	—

The total π-moment

$$\mu=\mu_1+\mu_7+\mu_2+\mu_3-\mu_c{}^*=0.575 \text{ a.u.}=1.46 \text{ D}$$

* μ_c represents the σ-core moment.

position of the oxygen atom, the positive pole lying at the oxygen nucleus.

Equivalent Orbitals of Dimethyl Ether. —The LCAO SCF MO method developed by Roothaan[14] will give the most reliable results for the electronic structure of a molecule. However, the low symmetry of the molecule of dimethyl ether prevents us from following this procedure. On the other hand, the unique treatment by Pople[15] of some simple molecules with lone pair electrons, such as water or ammonia, seems to express the electronic structures of these molecules quite well, though the results obtained by his method show that the lone pair moment may be overestimated. For example, in the case of water the lone pair moment obtained by Pople's method is about twice as large as that obtained by the LCAO SCF MO method[16]. This defect will be overcome by considering properly the apparent nuclear charge of oxygen as seen later.

Our treatment is similar to that by Pople and the values of the dipole moment used in our calculation are 1.30 D[8] and 0.30 D[2] for an ether molecule and a C–H bond, respectively. For the latter, its direction is assumed to be along the direction of the C–H bond with the negative center at the hydrogen atom. Outer electrons of $2s$ and $2p$ alone were considered explicitly and $1s$ inner electrons of the oxygen atom and the two carbon atoms were treated together with the nucleus as the rigid cores. Thus the nuclear charge of oxygen becomes 6 and that of carbon 1.059 upon the following approximations. For the orbitals of each carbon atom the sp^3 hybridization was a priori assumed. Moreover, to avoid complexity arising from the existence of methyl groups, each methyl group was replaced by a single C–H bond and its charge distribution was assumed to be expressed by point charges located at each nucleus with the distance of 1.09 Å. On these assumptions, the hybridization parameters at the oxygen atom and the coefficients in each bonding orbital were adjusted so as to be reconciled with the observed resultant moment. Such a simplification does not seem to be accompanied by any serious error within the limit of the approximation used here in the determination of wave functions.

TABLE IV. MOLECULAR CONSTANTS AND ATOMIC ORBITALS USED IN THE CALCULATION OF EQUIVALENT ORBITALS OF DIMETHYL ETHER, AND THEIR CALCULATED RESULTS

Molecular constants: Bond distance O–C 1.43Å; Bond angle 111°

Atomic orbitals:

$$\phi(2s)=(Z^5/3\pi)^{1/2}\ r\exp(-Zr)$$
$$\phi(2p)=(Z^5/\pi)^{1/2}\ r\cos\theta\ \exp(-Zr)$$

where $Z=2.275$ for the oxygen atom
$Z=1.625$ for the carbon atom

Equivalent orbitals

$$\chi(l_1)=\cos\varepsilon_l\phi(O_{2s})+\sin\varepsilon_l\phi(O_{2p_1})$$
$$\chi(l_2)=\cos\varepsilon_l\phi(O_{2s})+\sin\varepsilon_l\phi(O_{2p_2})$$
$$\chi(b_1)=\lambda\{\cos\varepsilon_b\phi(O_{2s})+\sin\varepsilon_b\phi(O_{2p_1})\}+\mu\psi(c_1)$$
$$\chi(b_2)=\lambda\{\cos\varepsilon_b\phi(O_{2s})+\sin\varepsilon_b\phi(O_{2p_2})\}+\mu\psi(c_2)$$

where

$$\psi(c_i)=1/2\{\phi(c_{i2s})+\sqrt{3}\,\phi(c_{i2p})\}$$

Acceptable values for the parameters:

$\lambda=0.665$ $\cos\varepsilon_b=0.367$ $\cos\varepsilon_l=0.508$
$\mu=0.475$ $\sin\varepsilon_b=0.929$ $\sin\varepsilon_l=0.860$
$\beta=110°$ $\gamma=108°$

The calculated total moment:

$$M=M_b+M_l+M_m{}^*=-8.89+2.80+7.43=1.34\text{D}$$

* M_m represents the moment of methyl group.

14) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
15) A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 218 (1953). See also, *Proc. Roy. Soc.*, **A202**, 323 (1950).
16) F. O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955); L. Burnelle and C. A. Coulson, *Trans. Faraday Soc.*, **53**, 403 (1957).; W. C. Hamilton, *J. Chem. Phys.*, **26**, 345 (1957).

The molecular constants and the atomic orbitals used in evaluating the necessary integrals are tabulated in Table IV together with the final results thus obtained, where the symbols used are the same as those employed by Pople, et al.[15] Necessary overlap integrals and dipole moment integrals are all found in the tables or the formulae given by Mulliken, et al.[17]

The distinction between the present results shown in Table IV and those by Duncan and Pople lies in the hybridization parameters at the oxygen atom. As pointed out by Pople, this discrepancy originates from the small overlap integral between $\phi(c_1)$ and $\phi(c_2)$ because of the comparatively long distance between the two carbon atoms of an ether molecule, and the larger Z-value of Slater's atomic orbital of carbon.

The Induced Polarization of the π-Electrons of Phenol.—The induced polarization due to the lone pair field was easily calculated by means of the first order perturbation theory based on the equivalent and the molecular orbitals already given. The geometrical configuration of the complex between a proton donating molecule and an accepting one is not clear enough for the present case. However, it is well known that in ice a tetrahedral arrangement prevails and its arrangement has the large electrostatic energy[18] and the large overlap integral which is concerned largely with the delocalization energy[19]. It seems, therefore, probable to assume that the three atoms, O–H···O lie on a straight line, though the thermal motion will, in fact, induce some deviation. Moreover the distance between the oxygen atom of phenol and that of ether is not measured in solution. But according to the relationship proposed by Nakamoto, Margoshes and Rundle[20] between the atomic distance and the shift of the infrared absorption, the distance between the two oxygen atoms was estimated as being about 2.9 Å which is larger than that of ice. For the purpose of comparison, the perturbed wave functions of phenol were calculated in the case of three O···O internuclear distances of 2.7, 2.8 and 2.9 Å, respectively. The following two approximations were employed for this calculation. Firstly, only the interaction between the lone pair electrons of ether and the π-electrons of the oxygen atom of phenol was considered, and the interaction of the lone pair electrons with other π-electrons in the benzene ring of phenol was neglected. Molecular integrals required in this computation were obtained by making use of the formulae described in Roothaan's paper[21]. Secondly, an apparent nuclear charge of the oxygen atom of ether was determined by the point charge approximation. The apparent nuclear charges obtained at the three interatomic distances are as follows:

O···O distance, R	2.7	2.8	2.9
Z'	2.200	2.196	2.192

These large values of the apparent charges look curious, and may probably be due, as already stated, to the effect of overestimation of lone pair moments. It is believed that such a defect will be excluded if the same treatment as that of water by Ellison and Shull[16] is carried out. The extent of the interaction between the apparent nuclear charge of the oxygen atom of ether and the π-electrons of the oxygen atom of phenol was also estimated by Roothaan's formulae as before.

Finally we formulate the calculating procedure for the perturbed wave functions of phenol. The perturbation H' is given by

$$H' = 2\int \frac{\chi(l_i)\chi(l_i)}{r}\,d\tau - \frac{Z'}{r'}$$

The first term represents a coulombic potential due to the lone pair electrons of ether in the orbital, $\chi(l_i)$ which participates in the hydrogen bond, and the second is that due to the apparent nuclear charge Z' of the oxygen atom of ether. The first-order perturbed wave functions of phenol will then be expressed as

$$\chi_i^{(1)} = \chi_i + \sum_{j\neq i} \frac{H'_{ij}}{E_i - E_j}\chi_j, \quad \begin{pmatrix} i=1,7,3 \\ j=1,7,3,5,6 \end{pmatrix}$$

Values of the π-moments calculated from these orbitals are tabulated in Table V at each internuclear separation.

This table shows that the polarization of the π-orbitals arising from the lone pair field is the order of a magnitude of 0.1 D compared with the value of about 0.2 D given by Hampson and Weissberger[22], who

17) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, ibid., **17**, 1248 (1949).
18) W. G. Schneider, ibid., **23**, 26 (1955); W. S. Fyfe, ibid., **21**, 2 (1953).
19) H. Tsubomura, This Bulletin, **27**, 445 (1954).
20) K. Nakamoto, M. Margoshes and R. E. Rundle, *J. Am. Chem. Soc.*, **77**, 6480 (1955).
21) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).
22) G. C. Hampson and A. Weissberger, *J. Chem. Soc.*, **1936**, 393.

TABLE V. MOMENTS OF THE PERTURBED π-ORBITALS OF PHENOL

At 2.7 Å $\mu = \mu_1 + \mu_7 + \mu_2 + \mu_3 + \mu_c$
$= 3.704 + 9.946 + 10.632 + 8.250 - 31.896$
$= 0.637$ a.u. $= 1.62$ D

At 2.8 Å $\mu = 3.647 + 9.970 + 10.632 + 8.277 - 31.896$
$= 0.630$ a.u. $= 1.60$ D

At 2.9 Å $\mu = 3.615 + 9.980 + 10.632 + 8.92 - 31.896$
$= 0.624$ a.u. $= 1.58$ D

The increment of π-moment, $\Delta\mu_\pi$

R in Å	2.7	2.8	2.9
μ in D	0.16	0.14	0.12

estimated the induced moment of the π-electrons due to a polar substituent group by making use of the average polarizability of the molecule. The induced moment decreases almost linearly with the increase of the interatomic distance from 2.7 to 2.9 Å. When we extrapolate it to the distance of 3.5 Å which corresponds to the sum of the van der Waals radii of both the oxygen atom of ether and the O–H of phenol, then the value obtained will be zero. These results show quite well that the theoretical treatment already described is reasonable. But it must be noted that the numerical values thus obtained are those of the interacting molecules which are placed mutually in the fixed configuration.

The Increment of the Dipole Moment Arising from Delocalization.—As is well known, the structures largely contributing to hydrogen bonding are considered as the following three:

[I] O–H O

[II] O⁻H⁺O

[III] O⁻H–O⁺

If we suppose that the ratio of the weights of structures I and II is of the same as that in a free state, then the increase of the dipole moment due to hydrogen bonding will be attributable only to the participation of the structure III. Strictly speaking, the transitional structures also must be taken into account. But it is difficult to treat them without making more precise quantum mechanical calculations. Neglecting these transitional structures, we can easily estimate the weight of the structure III from the additional moment observed.

One obstacle remains as yet. That is the direction of the resultant moment of the molecule in the free state. However, in view of the result[16] that the O–H bond moment in a water molecule is not so large as hitherto believed, it is assumed that only the lone pair dipoles make a contribution to the molecular dipole moment of benzyl alcohol. In the case of phenol, the direction of the resultant moment, as usually done, is determined by vectorial combination of dipole moments of both phenol itself and some of *p*-substituted phenols. The result[3] obtained shows that the direction of the resultant vector of phenol makes an obtuse angle of 91° with the O–C bond.

Once the direction of the resultant moment in the free state for benzyl alcohol and phenol, respectively, and the value of the induced moment of phenol in the bonded state are determined, then it is possible to calculate the increment of dipole moment, $\Delta\mu_D$ only due to delocalization.

Firstly, let us discuss the system of benzyl alcohol-dioxane. The bond angle about the oxygen atom of benzyl alcohol was taken to be 110°. Then, the value of $\Delta\mu_D$ obtained from the method mentioned above amounts to 0.10 D. When the interatomic distance between the two oxygen atoms is taken to be 3.0 Å from the shift of the infrared absorption[10], we obtain 14.41 D as the moment referring to the structure III, and its weight is estimated as about 0.7%.

Next, let us consider the system of phenol-dioxane. As the sp^2 hybridization was assumed for the orbitals of the oxygen atom, the bond angle about it was taken to be 120°. The interatomic distance between the two oxygen atoms was estimated as 2.9 Å as already stated. If the value of 0.12 D is used for the induced polarization of the π-electrons as already tabulated, $\Delta\mu_D$ is calculated as 0.21 D. This value corresponds to 1.5% as the weight of the structure III. Although it is qualitatively understood from the viewpoint of acidity that the contribution of the structure III in the latter system is about twice as large as that in the former, further discussion on this point will be given in the forthcoming report together with other data.

Summary

The dielectric measurements for the system of benzyl alcohol-dioxane and that of phenol-dioxane, respectively, were carried out by using benzene as the solvent.

The induced polarization of the π-electrons in the latter system was evaluated based on some assumptions. From these,

the additional moments due to delocalization were estimated and the weights of the structure III were evaluated for both systems.

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γ-Hydroxyarginine, a New Guanidino Compound from a Sea-cucumber. I. Isolation and Identification

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In the course of studies[1] on the extractable naturally occurring guanidino compounds by means of paper chromatography using Makisumi's method[2], the author found an unknown guanidino compound from the extract of a sea-cucumber, *Polycheira rufescens*, and isolated it as a hydrochloride. It was hydrolyzed, though somewhat more slowly than arginine, but completely by the action of arginase, into urea and an unknown amino compound. In 1953, Robin[3] oxidatively prepared γ-guanidinobutyric acid from L-arginine with the action of a homogenate obtained from the hepatopancreas of *Mytilus edulis*. The homogenate from this species appears to contain L-amino acid oxidase only as amino acid oxidase[4]. The isolated compound could also be converted enzymically and chemically into its oxidation products whcih were positive for the Sakaguchi reaction. Further characterizations of the isolated compound and its degradation products led the author to assume the unknown guanidino compound to be γ-hydroxyarginine. Consequently, the unknown amino compound produced from the isolated compound by the action of arginase should be γ-hydroxyornithine.

On the other hand, γ-hydroxyornithine was synthesized according to Tomita's method[5] which was somewhat modified by the author and then transformed into γ-hydroxyarginine by guanidization with S-methylisothiourea. The provisional structures of the isolated guanidino compound and the amino compound produced therefrom were proved to be correct by comparing them on a paper chromatogram with the synthetic γ-hydroxyarginine and γ-hydroxyornithine, respectively.

1) H. Sasaki, Y. Fujita, S. Makisumi and S. Shibuya, *J. Jap. Biochem. Soc.* (*Seikagaku*), **30**, 642 (1958).
2) S. Makisumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 737 (1952).
3) Y. Robin, *Bull. Soc. Chim. Biol.*, **35**, 285 (1953).
4) H. Blaschko and D. B. Hope, *Biochem. J.*, **62**, 335 (1956).
5) M. Tomita, *Z. physiol. Chem.*, **158**, 58 (1926).

Experimental

Isolation of the Unknown Guanidino Compound.—The sea-cucumbers used as the material were collected at the tidal zone near the Amakusa Marine Laboratory, the Faculty of Science, Kyushu University. The washed materials (43.5 kg.) removed from their internal organs were chopped in a meat-chopper and introduced into hot water (45 l., 70~80°C) for the purpose of extraction for 2 hr. with stirring. The residue separated from the extract was re-extracted in the same manner. The combined extract, deproteinized with a hot saturated basic lead acetate solution and freed from the lead, was passed through a column of Amberlite IR-120 (H- form). After washing the column with water, the adsorbed fraction was eluted with 2 N aqueous ammonia. The eluate, after removal of the ammonia by evaporation in vacuo, was again passed through a column of Amberlite IR-120 (ammonium form) to adsorb basic substances only. The elution from the washed column was carried out by using the same aqueous ammonia. The eluate freed from the ammonia was made up to 300 ml. with water and neutralized with 6 N hydrochloric acid. The solution, after addition of flavianic acid (50 g.), was heated for 30 min. on a boiling water bath. When the resulting solution was allowed to stand overnight in an

ice-box, a flavianate crystallized out. The flavianate was separated and washed with a small amount of cold water. It consisted almost entirely of the unknown guanidino compound, except for slight contamination with arginine. The product was recrystallized from hot water, until its paper chromatogram showed only one spot with the Sakaguchi or ninhydrin reaction. The purified flavianate was dissolved in hot water (100 ml.), and it was treated with a barium hydroxide solution to remove the flavianic acid moiety in the usual manner. The filtrate freed from the excessive barium was evaporated up to dryness in vacuo. The residue was extracted repeatedly with 50% hot ethanol. The extract, after evaporation to dryness, was dissolved in water (50 ml.), and the resulting solution was brought to pH 6~7 with 1 N hydrochloric acid. It was decolorized with charcoal and concentrated to a syrup in vacuo. The syrup was dissolved in 50% hot ethanol (10 ml.), and then absolute ethanol was added to it until the solution became opalescent. When the solution was kept overnight in a refrigerator, colorless plate crystals of the guanidino compound appeared. The compound was dissolved in a minute amount of 70% hot ethanol and then recrystallized with the addition of absolute ethanol. The yield was about 2.7 g.; m.p. 190~191°C (decomp.); $[\alpha]_D^{23}$ +5.4° (c 2, in 5 N hydrochloric acid).

Anal. Found: C, 31.75; H, 6.95; N, 24.65; Cl, 15.68. Calcd. for $C_6H_{11}N_4O_3 \cdot HCl$: C, 31.79; H, 6.67; N, 24.72; Cl, 15.64%.

It gave the Sakaguchi, the Lieben (iodoform), and ninhydrin reaction, indicating the presence of guanidino, alcoholic hydroxy (on the basis of the hydrogen content, alcoholic hydroxy group is superior to ketonic), and amino groups, respectively.

Enzyme Actions on the Guanidino Compound.—*1. Arginase.*—The arginase used in this experiment was a partially purified beef liver preparation of Step D according to Greenberg[6]. The guanidino compound was incubated to hydrolyze with arginase at pH 9.5 and 35°C for 24 hr. The incubate, after deproteinization with basic lead acetate, was fractionally purified by using Amberlite IR-120 (H- and ammonium forms). Since the purified fraction obtained here showed only one spot on a paper chromatogram with ninhydrin reaction, it was not necessary to carry out further purification. The fraction was decolorized with charcoal and crystallized similarly as in the case of isolation of the guanidino compound. The yield of the recrystallized compound was 280 mg. from 500 mg. of the guanidino compound; m.p. 183°C (decomp.); $[\alpha]_D^{32}$ +21.0° (c 2, in water).

Anal. Found: C, 32.65; H, 6.86; N, 15.2.1 Calcd. for $C_5H_{12}N_2O_3 \cdot HCl$: C, 32.58; H, 7.10; N, 15.17%.

This gave ninhydrin- and iodoform reaction but not the Sakaguchi reaction. The effluent passed through a column of Amberlite IR-120 (H^+ form) was again passed through a column of Amberlite (OH^- form), and from this effluent urea was identified as dixanthylurea and urea nitrate.

2. L-Amino acid oxidase.—The guanidino compound was incubated with the enzyme preparation obtained from the hepatopancreas of *Mytilus edulis* according to Robin's method[3] at pH 6.2 and 35°C for 24 hr. under aeration. The incubate acidified with acetic acid to pH 3~4 was boiled for 10 min. and filtered. To the filtrate (200 ml.) was added 30% hydrogen peroxide (1 ml.) for further oxidation of the keto acid to be produced by oxidative deamination from the guanidino compound, and it was allowed to stand for 15 hr. at room temperature. In this condition the guanidino compound itself is not oxidized at all with hydrogen peroxide. The resulting solution was passed through a column of Amberlite IR-120 (H-form), the column was washed with water, and then the adsorbed oxidation product was eluted from it by using 2 N aqueous ammonia. The eluate was evaporated up to dryness, and the residue was dissolved in 50% hot ethanol. When the solution was cooled in an ice-box, colorless needle crystals of the product appeared. The yield was 100 mg. from 300 mg. of the material; m.p. 238~240°C (decomp.); $[\alpha]_D^{22}$ −15.5° (c 2, in 5 N hydrochloric acid).

Anal. Found: C, 37.26; H, 6.88; N, 26.08. Calcd. for $C_5H_{11}N_3O_3$: C, 37.25; H, 7.11; N, 26.25%.

This compound gave the Sakaguchi and iodoform reaction, but not ninhydrin reaction.

Identification of the Oxidation Product.—*1. Reduction with hydroiodic acid.*—The oxidation product (10 mg.) was heated with hydroiodic acid (d=1.7, 0.5 ml.) for 2 hr. at 140°C in a sealed tube. After removal of the hydroiodic acid, the solution was tested by paper chromatography. On the basis of the result, it was found that the product was reduced to a compound which was identified as γ-guanidinobutyric acid (Table I).

TABLE I. R_f VALUES OF REDUCTION PRODUCT WITH HYDROIODIC ACID AND γ-GUANIDINOBUTYRIC ACID

	Solvent			
	I	II	III	IV
Reduction product	0.55	0.52	0.62	0.43
γ-Guanidinobutyric acid	0.55	0.52	0.62	0.43

One dimensional ascending method. Toyo-Roshi No. 52. Solvent: I, *n*-Butanol : Acetic Acid : Pyridine : Water = 40 : 10 : 10 : 20 (vol. %); II, *n*-Butanol : Acetic Acid : Pyridine : Water=30 : 6 : 24 : 20(vol. %); III, *n*-Butanol : Acetic Acid : Water=40 : 10 : 20 (vol. %); IV, *n*-Propanol : Water=70 : 30 (vol. %).

The R_f values shown in Tables II and III were also obtained by using the same procedures.

2. Comparison with the synthetic γ-guanidino-β-hydroxybutyric acid.—In a preliminary experiment, it was observed paper-chromatographically

6) D. M. Greenberg, "The Enzymes", vol. I, edited by J. B. Sumner and K. Myrbäck, Academic Press Inc., New York (1951), p. 905.

that the naturally occurring guanidino compound was oxidatively degraded with barium permanganate to guanidine and glycocyamine by way of an intermediate which was later proved to be identical with the oxidation product formed by the action of L-amino acid oxidase. The production of glycocyamine led to the conclusion that the alcoholic hydroxy group should situate in β- or γ-, probably γ-position, but not δ-position of the guanidino compound; accordingly, the structure of the enzymatic oxidation product before reduction by hydroiodic acid is to be γ-guanidino-β-hydroxybutyric acid. The conclusion was supported satisfactorily by comparing the paper chromatographic behaviors of the oxidation product with those of the synthetic γ-guanidino-β-hydroxybutyric acid[7,8] (Table II).

TABLE II. R_f VALUES OF OXIDATION PRODUCT WITH OXIDASE AND γ-GUANIDINO-β-HYDROXYBUTYRIC ACID

	Solvent			
	I	II	III	IV
Oxidation product	0.40	0.38	0.48	0.35
γ-Guanidino-β-hydroxybutyric acid	0.40	0.38	0.48	0.35

Synthesis of γ-Hydroxyornithine.—Finely powdered sodium ethyl acetylaminomalonate (24 g.) and γ-phthalimido-β-hydroxypropyl chloride (24 g.) were thoroughly mixed, and the mixture was heated at 140~150°C for 5 hr. with vigorous stirring. To the extremely viscous reaction mixture was added concentrated hydrochloric acid (100 ml.), and it was refluxed for 10 hr. and then allowed to stand overnight. The filtrate removed from the phthalic acid was concentrated in vacuo. Dilution with water and evaporation in vacuo were repeated three times to remove the excess of hydrochloric acid as much as possible. The syrup obtained thus was dissolved in water (200 ml.), and from this solution a basic fraction was separated by using Amberlite IR-120 (H- and ammonium form) in the same manner as described in the isolation procedures for the guanidino compound. The basic fraction, after being passed through a column of finely powdered Amberlite IR-120 (ammonium form, 100~200 mesh, 3 cm. × 40 cm.), was fractionally eluted and collected as follows. The column was washed with water, and the adsorbed substances were developed and eluted with 0.2 N aqueous ammonia. The eluate collected between 350 and 650 ml. was concentrated to a syrup in vacuo. The syrup was dissolved in a small amount of water, and the solution was adjusted to pH 6~7 with 1 N hydrochloric acid, decolorized with charcoal, and again concentrated to a syrup in vacuo. The syrup dissolved in a small amount of 50% hot ethanol was subjected to crystallization in an ice-box with the addition of absolute ethanol. After 2 days, the crystals of γ-hydroxyornithine hydrochloride were obtained. Yield, 8%; m. p. 181~183°C (decomp.).

Anal. Found: C, 32.72; H, 7.30; N, 15.65. Calcd. for $C_5H_{12}N_2O_3 \cdot HCl$: C, 32.53; H, 7.10; N, 15.17%.

Synthesis of γ-Hydroxyarginine.—γ-Hydroxyornithine hydrochloride (370 mg.) and S-methylisothiourea (280 mg.) were dissolved in 1 N sodium hydroxide (5 ml.). The solution which had been left to stand for 5 days at room temperature was passed through a column of Amberlite IR-120 (H- form). After washing the column with water, the adsorbed compounds were eluted with 2 N ammonia. The eluate was evaporated up to dryness in vacuo and the residue was dissolved in water (10 ml.). The solution was heated on a boiling water bath for 30 min. with the addition of flavianic acid (2 g.). On keeping the solution for 2 days in an ice-box, a flavianate of γ-hydroxyarginine crystallized out. The flavianate, after removal of the flavianic acid moiety in the usual manner, was converted into γ-hydroxyarginine hydrochloride. Yield, 57%; m. p. 189~190°C (decomp.).

Anal. Found: C, 31.88; H, 6.76; N, 24.83. Calcd. for $C_6H_{14}N_4O_3 \cdot HCl$: C, 31.79; H, 6.67; N, 24.72%.

Comparison of the Naturally Occurring Guanidino and Amino Compounds with the Synthetic Ones.—The synthetic γ-hydroxyarginine and γ-hydroxyornithine showed the same paper chromatographic behaviors as those of the naturally occurring guanidino compound and the amino compound produced therefrom by the action of arginase as shown in Table III.

TABLE III. R_f VALUES OF NATURALLY OCCURRING GUANIDINO AND AMINO COMPOUNDS AND SYNTHETIC ONES

	Solvent			
	I	II	III	IV
Guanidino compound	0.16	0.19	0.20	0.17
γ-Hydroxyarginine	0.16	0.19	0.20	0.17
Amino compound	0.12	0.15	0.17	0.13
γ-Hydroxyornithine	0.12	0.15	0.18	0.13

Summary

A new guanidino compound was isolated from a sea-cucumber, *Polycheira rufescens*, and identified as γ-hydroxyarginine. γ-Hydroxyornithine and γ-guanidino-β-hydroxybutyric acid produced enzymically from the guanidino compound were also isolated and identified. It was, further, concluded that the new guanidino compound susceptible to arginase and L-amino acid oxidase should be γ-hydroxy-L-arginine, although the configuration of the γ-hydroxy group was not yet decided.

The author wishes to express his cordial thanks to Professor S. Shibuya for his guidance and encouragement, to Assistant

7) M. Tomita, *Z. physiol. Chem.*, **124**, 253 (1923).
8) T. Fukagawa, ibid., **231**, 203 (1935).

Professor N. Izumiya for his advice, and to Messrs. S. Makisumi, S. Ouchi, T. Yamashita, R. Yamada, M. Ono, T. Kamata and Y.Ishikawa for their assistance with the collection of sea-cucumbers. His thanks are also due to the Ministry of Education for financial support of this research.

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Formation and Aging of Precipitates. XII. Studies on Types of Crystal Growth of Barium Sulfate by Dissolution in Water*

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Barium sulfate is one of the sparingly soluble salts and it gradually dissolves in water. The investigation of dissolution of barium sulfate in EDTA solution was reported[1], but hitherto no morphological study has been made. The author previously reported the investigation of growth process of barium sulfate precipitate[2]. The precipitate was purified by the diffusion washing, that is, a drop containing the precipitate was placed on a Formvar film floating on the surface of distilled water for about ten minutes and the soluble matter was made to diffuse through the film into the water below. About ten minutes were suitable for the washing process while, under too long time of washing, the precipitate tended to dissolve in water. The present investigation is intended to study the type of crystal growth of barium sulfate by the dissolution of the crystal under the diffusion washing for a long period.

Sample.—Two kinds of barium sulfate precipitates were used in the dissolution by diffusion washing. One was the oval particles prepared by the method described in the previous paper[3], and the other was the thin rectangular particles prepared by direct mixing of dilute reagents[4].

Experimental.—A drop of the suspension containing the precipitate mentioned above was placed on a thin Formvar film floating on the surface of distilled water. The drop was left for several hours or one day to let ions diffuse from the drop into the water below. The film was then scooped up with a specimen grid for electron microscopy. Both the fresh and the aged precipitates were examined.

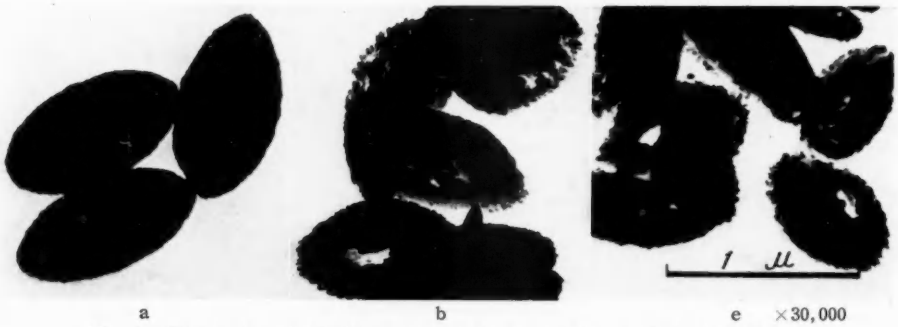
Experimental Results and Consideration

Oval Crystal. — The freshly prepared oval particles as shown in Fig. 1a changed to those as shown in Figs. 1b and c after they were treated with water for three hours. The radial arrangement of small particles are observed in each oval particles. It seems that the oval particles, subjected to dissolution, have been formed by the repetition of dendritic growth, the rate of which is rapid and slow alternately, and that the weakly oriented parts around the particles dissolve in water easily while the comparatively stable parts are not easily soluble, thus the radially arranged particles can be observed. Several hours after, the oval particles dissolved in water and changed in appearance as shown in Figs. 2a and c. The particle shown in Fig. 2a has still the original orientation of crystal structure and the orientation of crystal shown in Fig. 2c was disordered, as was proved by electron diffraction pattern shown in Figs. 2b and d.

Oval particles which were aged for about one day in the mother liquid changed in appearance as shown in Figs. 3a and b. In the aging process, the crystal structure of particles, especially that of the surface of particles, seems to become perfect gradually. Thus in the case of an aged particle, the inner part

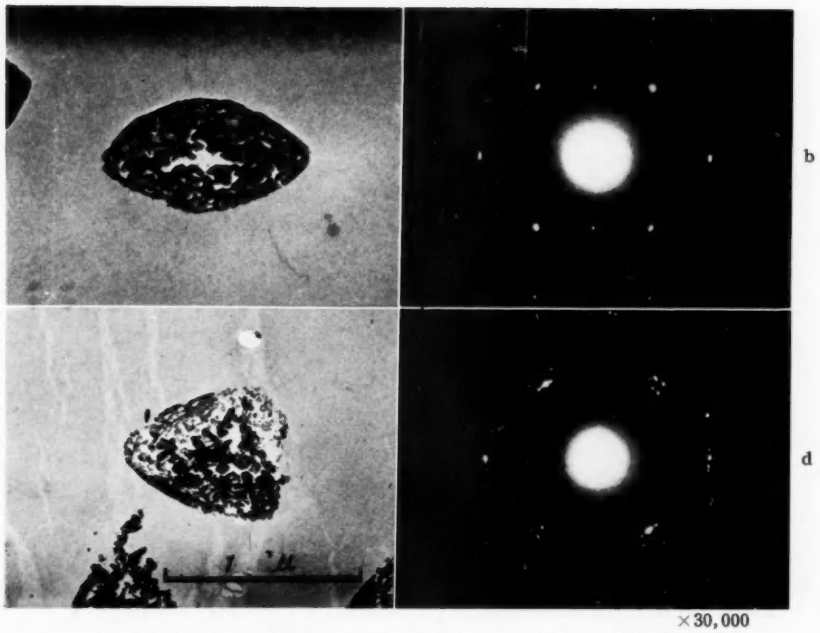
* The eleventh paper of this series, This Bulletin, **32**, 387 (1959).

1) K. Mukai and K. Goto, *Japan Analyst (Bunseki Kagaku)*, **6**, 732 (1957).
2) K. Takiyama, This Bulletin, **31**, 950 (1958).
3) K. Takiyama. ibid., **32**, 387 (1959).
4) K. Takiyama, ibid., **27**, 121 (1954); **32**, 68 (1959).



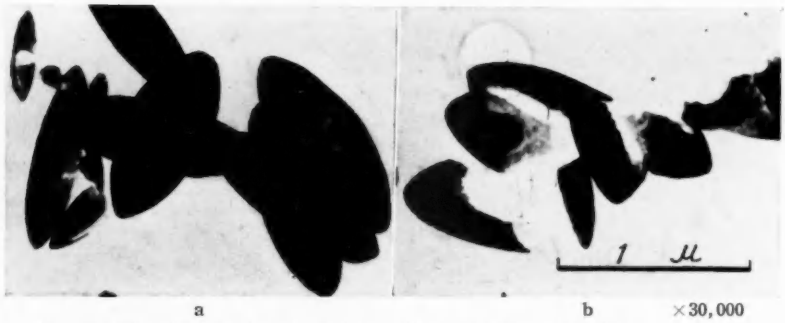
a b c ×30,000

Fig. 1. Dissolution of freshly prepared barium sulfate particles in water.
a: original particles; b, c: after treatment for three hours



×30,000

Fig. 2. Dissolution of freshly prepared barium sulfate particles by treatment with water for six hours.



a b ×30,000

Fig. 3. Dissolution of aged barium sulfate particles in water.
a: after treatment for three hours; b: after treatment for six hours

a b c ×30,000

Fig. 4. Dissolution of freshly prepared barium sulfate particles by treatment with water for three hours.

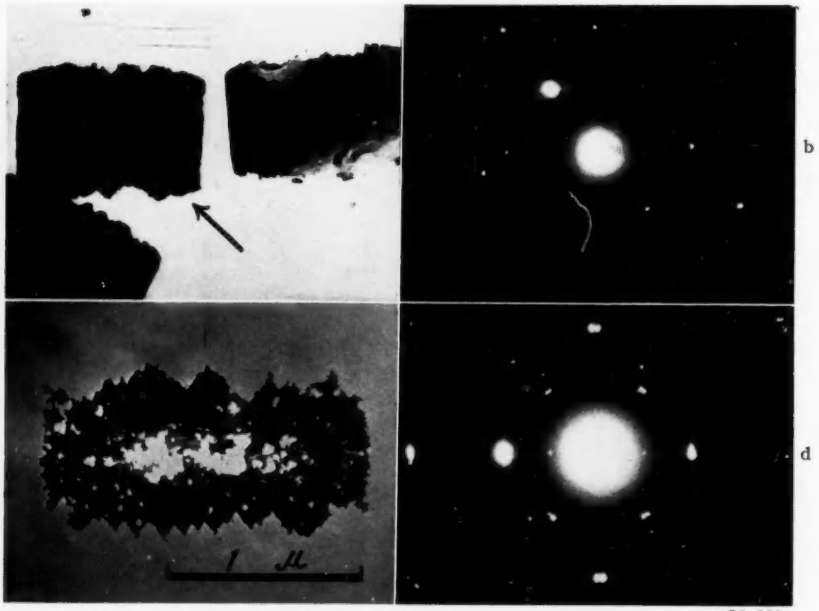


Fig. 5. Dissolution of aged barium sulfate particles in water.
a, b: after treatment for six hours
c, d: after treatment for one day

of particle dissolved faster than the surface part which remained undissolved as shown in Fig. 3b.

Rectangular Thin Crystal.—Freshly prepared rectangular particles dissolved from the corner of particles as shown in Fig. 4. The corner of the slightly dissolved particles has many steps as shown in Figs. 4b and c. The rectangular particles are the perfect single crystal as described in the previous paper[4] and their growth seems to agree with the perfect crystal growth theory proposed by Kossel and Stranski[5]. Thus the particles seem to have grown stepwise and to have many steps which are large in some parts. Then weak parts at the surface of particles dissolved quickly and many of these large steps appeared around the particles.

The aged rectangular perfect crystals dissolved in water and gave the figure as shown in Fig. 5. The particles began to dissolve from the side of crystals, that is, from (0 1 0) plane (Fig. 5a), and the inner parts dissolved faster than the surface parts of particles (Fig. 5c). The surface of aged particles seems to become stable by complete orientation of crystal structure during digestion in mother liquid as in the case of oval particles. The particle shown in Fig. 5a (arrow) has a perfect single crystal structure (Fig. 5b) and the single crystal structure of the particle shown in Fig. 5c has begun to decompose (Fig. 5d) as examined by electron diffraction method. The crystal structure of the surface part remained almost perfect even after one day's treatment with water.

5) I. M. Stranski, *Z. phys. Chem.*, **136**, 259 (1928).

Summary

The oval and rectangular crystals of barium sulfate precipitates seem to grow through the dendritic and perfect crystal growth processes, respectively. These particles dissolve in the process of diffusion washing. The oval particles dissolved slightly show the dendrite structure in them, and the rectangular particles dissolved slightly show the large steps around the particles. Thus these particles proved to have grown through dendritic and perfect crystal growth processes, respectively. The surface of the aged particles of both oval and rectangular crystals become stable by digestion in mother liquid; hereby the dissolution rate of inner parts of particles is faster than that of surface parts of them.

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Electronic Structures of Naphthalenediols. I. α,α'-Naphthalenediols

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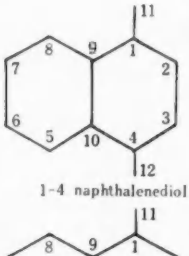
While the electronic structures of substituted benzenes have been studied by many authors, the theoretical investigations of those of substituted naphthalenes have been scarcely ever made[1-4], because of difficulties of the calculation due to low symmetry of these molecules and the presence of many π-electrons to be considered. The spectra of naphthalene mono-derivatives show[5] in general two kinds of characteristic picture depending upon the position of substitution, either β or α positions. In the di-derivatives, two substituents are bonded with rings in two ways, that is, both with the same

1) H. Baba and T. Suzuki, Symposium on the Electronic Structures of Molecules, held at Kyoto, 1958.
2) R. Daudel and M. Martin, *Bull. soc. chim. France*, **1948**, 559; ibid., **1949**, 83.
3) D. Peters, *J. Chem. Soc.*, **1957**, 646, 1993.
4) B. Pullman, *Bull. soc. chim. France*, **1948**, 533.
5) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", Jone Wiley and Sons, New York, (1951).

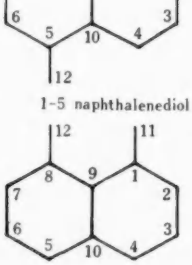
ring and each with the different rings. This seems to lead additional effects on their molecular properties. De Laszlo[6] showed that fourteen isomeric dichloronaphthalenes could be classified spectroscopically as aa, ab and bb compounds. But as pointed out by Daglish[7] in the case of naphthalene di-derivatives having strongly conjugating substituents, such as hydroxyl, amine etc., this classification is an over-simplification of the problem. In the present paper theoretical treatments based on the simple MO theory will be applied to the electronic structures of α,α'-naphthalenediols, such as 1-4, 1-5 and 1-8 diols, in order to establish the effects of substituents on their molecular properties. The electronic structures of β,β'-naphthalenediols will be considered in the next paper.

Method of Calculation.—The method is based on the simple LCAO MO theory with only fourteen $2p\pi$ electrons considered explicitly. The Coulomb and the exchange integrals used are the same as those in the previous paper[8], where the electronic structure of phenol was discussed. All the Coulomb integrals for carbon atoms are taken as equal to α. When the non-uniformity of charge distribution is small, the above assumption may be approximately held. In order to simplify the calculation we make this approximation. The numbering of atoms and the symmetry orbitals for the moleclues are shown in Fig. 1. A, B, A_2 and B_1 in the figure express the irreducible representations, to which each symmetry orbital belongs.



1-4 naphthalenediol

B_1 $\sigma_1=\phi_1+\phi_4$ A_2 $\sigma_7=\phi_1-\phi_4$
$\sigma_2=\phi_2+\phi_3$ $\sigma_8=\phi_2-\phi_3$
$\sigma_3=\phi_5+\phi_8$ $\sigma_9=\phi_5-\phi_8$
$\sigma_4=\phi_6+\phi_7$ $\sigma_{10}=\phi_6-\phi_7$
$\sigma_5=\phi_9+\phi_{10}$ $\sigma_{11}=\phi_9-\phi_{10}$
$\sigma_6=\phi_{11}+\phi_{12}$ $\sigma_{12}=\phi_{11}-\phi_{12}$



1-5 naphthalenediol

A $\sigma_1=\phi_1+\phi_5$ B $\sigma_7=\phi_1-\phi_5$
$\sigma_2=\phi_2+\phi_6$ $\sigma_8=\phi_2-\phi_6$
$\sigma_3=\phi_3+\phi_7$ $\sigma_9=\phi_3-\phi_7$
$\sigma_4=\phi_4+\phi_8$ $\sigma_{10}=\phi_4-\phi_8$
$\sigma_5=\phi_9+\phi_{10}$ $\sigma_{11}=\phi_9-\phi_{10}$
$\sigma_6=\phi_{11}+\phi_{12}$ $\sigma_{12}=\phi_{11}-\phi_{12}$

1-8 naphthalenediol

B_1 $\sigma_1=\phi_1+\phi_8$ A_2 $\sigma_8=\phi_1-\phi_8$
$\sigma_2=\phi_2+\phi_7$ $\sigma_9=\phi_2-\phi_7$
$\sigma_3=\phi_3+\phi_6$ $\sigma_{10}=\phi_3-\phi_6$
$\sigma_4=\phi_4+\phi_5$ $\sigma_{11}=\phi_4-\phi_5$
$\sigma_5=\phi_9$ $\sigma_{12}=\phi_{11}-\phi_{12}$
$\sigma_6=\phi_{10}$
$\sigma_7=\phi_{11}+\phi_{12}$

Fig. 1. Numbering of atoms and symmetry orbitals.

Results and Discussion

(A) MO's and their Polarization.—The calculated MO's and their energies for the naphthalenediols are summarized in Table I.

The comparison of the MO's of the naphthalene[9] and those of diols obtained here makes it clear that the signs of the coefficients at each carbon AO in each MO are unchanged by the introduction of the hydroxy groups. Thus, so far as the mono- and di-derivatives are concerned, it is not too much to say that the effect of substitution brings about some modification of the MO's of parent hydrocarbon, but the extent of these modifications is not so large as to destroy their orbital characteristics. This situation will give a basis to the assumption that in many cases the perturbation theory supplies qualitatively useful results, even if the effect of the substitution amounts to considerable extent. In the naphthalene molecule, φ_1 is totally symmetric for the symmetry operation with respects to the principal axis and has no node of the wave function. For the naphthalenediols, φ_1's of them have still no node, but they are strongly polarized along the direction toward the substituents in a regular manner. If we try to measure the degree of polarization by the value of $C_{1\mu}/C_{1\mu_0}$, where the $C_{1\mu}$ is the square of coefficient at μ-th carbon AO in φ_1 of the diol and the $C_{1\mu_0}$ is that of naphthalene, these values are the greatest at the carbon atoms bonded with a hydroxy group and decrease with the increase in the distance between the μ-th carbon atom and the substituent. For the case of 1-8 diol, the values at the carbon atoms numbered by 1, 2, 3 and 4 in Fig. 1 are 1.367, 0.925, 0.656 and 0.591, respectively. This polarization is similar to the inductive effect which is usually regarded as the polarization of σ-cores

6) H. de Laszlo, *J. Am. Chem. Soc.*, **50**, 892 (1928).
7) C. Daglish, ibid., **72**, 4859 (1950).
8) K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).
9) B. Pullman and A. Pullman, "Les Theories electroniques de la Chimie organique", Masson et Cie, Paris, (1952), p. 199.

TABLE I. MO'S AND MO ENERGIES

Symmetry	Orbital energy in β	MO
		1-4-naphthalenediol
B_1	2.4227	$\varphi_1=0.3452\sigma_1+0.2426\sigma_2+0.2386\sigma_3+0.1677\sigma_4+0.4103\sigma_5+0.2619\sigma_6$
A_2	1.9264	$\varphi_2=0.3498\sigma_7+0.1195\sigma_8-0.0962\sigma_9-0.0329\sigma_{10}+0.1524\sigma_{11}+0.5742\sigma_{12}$
B_1	1.8058	$\varphi_3=0.1695\sigma_1+0.2103\sigma_2-0.3111\sigma_3-0.3860\sigma_4-0.1757\sigma_5+0.3877\sigma_6$
B_1	1.3271	$\varphi_4=0.1246\sigma_1+0.381\sigma_2-0.0796\sigma_3-0.2433\sigma_4+0.1377\sigma_5-0.5048\sigma_6$
A_2	1.1082	$\varphi_5=0.1631\sigma_7+0.0774\sigma_8-0.4849\sigma_9-0.2300\sigma_{10}+0.3074\sigma_{11}-0.2914\sigma_{12}$
B_1	1.0000	$\varphi_6=0.4083(\sigma_2+\sigma_4-\sigma_5)$
A_2	0.4321	$\varphi_7=0.4276\sigma_7+0.2986\sigma_8+0.3096\sigma_9+0.2162\sigma_{10}+0.0824\sigma_{11}-0.2803\sigma_{12}$
B_1	−0.6922	$\varphi_8=0.3818\sigma_1-0.2256\sigma_2-0.4607\sigma_3+0.2722\sigma_4+0.0466\sigma_5-0.1219\sigma_6$
A_2	−1.0000	$\varphi_9=-0.4083(\sigma_8-\sigma_{10}-\sigma_{11})$
B_1	−1.3635	$\varphi_{10}=0.4369\sigma_1-0.1846\sigma_2+0.3574\sigma_3-0.1512\sigma_4-0.3361\sigma_5-0.1069\sigma_6$
A_2	−1.6396	$\varphi_{11}=0.2616\sigma_7-0.4090\sigma_8+0.2750\sigma_9-0.4299\sigma_{10}+0.0209\sigma_{11}-0.0584\sigma_{12}$
A_2	−2.3271	$\varphi_{12}=0.3158\sigma_7-0.2379\sigma_8-0.2901\sigma_9+0.2186\sigma_{10}-0.4565\sigma_{11}-0.0578\sigma_{12}$
		1-5-naphthalenediol
A	2.4190	$\varphi_1=0.3362\sigma_1+0.2195\sigma_2+0.1949\sigma_3+0.2519\sigma_4+0.4144\sigma_5+0.2561\sigma_6$
B	1.9945	$\varphi_2=0.3687\sigma_7+0.2472\sigma_8+0.1243\sigma_9+0.0007\sigma_{10}+0.1229\sigma_{11}+0.5219_{12}$
A	1.6212	$\varphi_3=0.1038\sigma_1-0.0407\sigma_2-0.1698\sigma_3-0.2346\sigma_4-0.2106\sigma_5+0.5994\sigma_6$
B	1.5296	$\varphi_4=-0.0084\sigma_7+0.2853\sigma_8+0.4447\sigma_9+0.3951\sigma_{10}-0.1594\sigma_{11}-0.1981\sigma_{12}$
B	1.0034	$\varphi_5=0.2897\sigma_7+0.2877\sigma_8-0.0010\sigma_9-0.2887\sigma_{10}+0.2887\sigma_{11}-0.4082\sigma_{12}$
A	1.0000	$\varphi_6=0.4083(\sigma_2+\sigma_3-\sigma_5)$
A	0.4590	$\varphi_7=0.3696\sigma_1+0.2900\sigma_2-0.2365\sigma_3-0.3985\sigma_4+0.0535\sigma_5-0.2484\sigma_6$
B	−0.7005	$\varphi_8=0.4268\sigma_7-0.2336\sigma_8-0.2632\sigma_9+0.4180\sigma_{10}+0.0296\sigma_{11}-0.1357\sigma_{12}$
B	−1.0000	$\varphi_9=-0.4083(\sigma_8-\sigma_9-\sigma_{11})$
A	−1.3550	$\varphi_{10}=0.3739\sigma_1-0.1062\sigma_2-0.2300\sigma_3+0.4178\sigma_4-0.3362\sigma_5-0.0917\sigma_6$
A	−1.6442	$\varphi_{11}=0.3159\sigma_1-0.4337\sigma_2+0.3972\sigma_3-0.2194\sigma_4-0.0365\sigma_5-0.0703\sigma_6$
B	−2.3269	$\varphi_{12}=0.3129\sigma_7-0.2313\sigma_8+0.2254\sigma_9-0.2931\sigma_{10}-0.4567\sigma_{11}-0.0572\sigma_{12}$
		1-8-naphthalenediol
B_1	2.4249	$\varphi_1=0.3513\sigma_1+0.2219(\sigma_2+2\sigma_5)+0.1868(\sigma_3+2\sigma_6)+0.2312\sigma_4+0.2659\sigma_7$
A_2	1.9360	$\varphi_2=0.3278\sigma_8+0.2662\sigma_9+0.1875\sigma_{10}+0.0969\sigma_{11}+0.5264\sigma_{12}$
B_1	1.7562	$\varphi_3=0.1794\sigma_1-0.0094(\sigma_2+2\sigma_5)-0.1959(\sigma_3+2\sigma_6)-0.3346\sigma_4+0.4903\sigma_7$
A_2	1.4410	$\varphi_4=0.0319\sigma_8+0.3116\sigma_9+0.4172\sigma_{10}+0.2895\sigma_{11}-0.3795\sigma_{12}$
B_1	1.0035	$\varphi_5=0.2977\sigma_1+0.1975(\sigma_2+2\sigma_5)-0.0995(\sigma_3+2\sigma_6)-0.2973\sigma_4-0.4198\sigma_7$
B_1	1.0000	$\varphi_6=0.4083(\sigma_2+\sigma_3-\sigma_5-\sigma_6)$
A_2	0.4666	$\varphi_7=0.3490\sigma_8+0.3283\sigma_9-0.1958\sigma_{10}-0.4197\sigma_{11}-0.2364\sigma_{12}$
A_2	−0.7020	$\varphi_8=0.4332\sigma_8-0.2077\sigma_9-0.2874\sigma_{10}+0.4094\sigma_{11}-0.1378\sigma_{12}$
B_1	−1.0000	$\varphi_9=-0.4083(\sigma_2-\sigma_3-\sigma_5+\sigma_6)$
B_1	−1.3573	$\varphi_{10}=0.3939\sigma_1-0.1557(\sigma_2+2\sigma_5)-0.1826(\sigma_3+2\sigma_6)+0.4035\sigma_4-0.0965\sigma_7$
A_2	−1.6416	$\varphi_{11}=0.2864\sigma_8-0.4255\sigma_9+0.4121\sigma_{10}-0.2511\sigma_{11}-0.0637\sigma_{12}$
B_1	−2.3273	$\varphi_{12}=0.3172\sigma_1-0.2325(\sigma_2+2\sigma_5)+0.2240(\sigma_3+2\sigma_6)-0.2887\sigma_4-0.0581\sigma_7$

caused by the introduction of the polar group into the molecule. But, when we take $\beta_{CO}=0$, this polarization is absent, so far as invoking the simple theory, since the interactions between the $2p\pi$ electrons of the substituents and of the naphthalene ring are impossible in this case. If the polarizations of φ_1's are inductive, it is expected that the value of C_{11}/C_{11_0} for 1-8-diols is the greatest and the smallest for 1-5-diol. Actually, their values are 1,367, 1,319 and 1.251 for 1-8, 1-4 and 1-5-diols, respectively. Although the all MO's for the diols have the same numbers of nodes as those for the corresponding naphthalene MO's, the regular polarizations are not recognized in them except φ_1's. In the light of the above fact, we may except that when the overlap between the electronic cloud of conjugated molecule and that of the attacking molecule is present, the lowest π-orbital of the former will be most sensitive to the influence of the latter. The occupied lowest π-orbital will, therefore, play the most important role for the rearrangement of charge distribution of the molecule produced by the approach of the reagent.

(B) Absorption Spectra. — It is well known that the introduction of the hydroxy group into the α-position of naphthalene causes a very large bathochromic shift in the p-band with some distortion of the fine structure and a rather small shift in the α-band. As mentioned by Daglish[7] and Spruit[10], the spectra of α, α'-diols also have those characteristic features, but these bathochromic shifts in the p-bands are larger in 1-5 derivative and slightly larger in 1-5 compound than that in α-naphthol. Comparison of the energy level diagrams given in Fig. 2

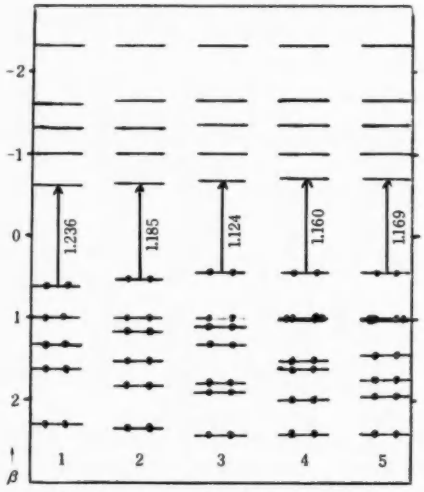


Fig. 2. Energy level diagrams.
1. naphthalene
2. α-naphthol
3. 1-4 naphthalenediol
4. 1-5 naphthalenediol
5. 1-8 naphthalenediol

makes it possible to expect that the spectra of 1-8 diol may be very close to that of 1-5 diol, since the spacing of their levels concerned with the electronic transitions in the near ultraviolet region are very similar to each other. This is the case of Hochstein et al.[11], who reported that the spectroscopic distinction between them was difficult. The energy level diagram of α-naphthol which is calculated by using the same parameters for diols is also given in Fig. 2. The numerical values given in Fig. 2 express the orbital energy differences between φ_7 and φ_8 for the corresponding compounds in the units of β, respectively. The comparison of these values suggests that the wave lengths of absorption corresponding to the $\varphi_7 \rightarrow \varphi_8$ transitions which are closely related to the p-band are in following order; 1-4 diol > 1-5 diol $\simeq$ 1-8 diol $\simeq$ α-naphthol.

The fact that the orbitals having orbital energies of $\pm\beta$ are not affected by the substitution in the α-positions of naphthalene may provide a determining factor for the discussion of electronic transitions concerned with α-bands of α-compounds, because these orbitals are closely connected with them. Experimentally observed distortion of the fine-structure in the p-band will be reasonably attributable to the anharmonicity produced by the ununiform charge distribution and the alteration of the bond orders. The full discussion about the electronic transitions on the ground of the method involving the electronic interaction will be desirable. Here, we will try no further discussion about this problem.

(C) Extra Delocalization Energies and Molecular Diagrams.—Delocalization of the $2p\pi$-electrons of substituents into the naphthalene ring brings the excess of stabilization energies (extra delocalization energies) for the molecule as a whole. These values per one hydroxy group are evaluated to be 0.1807, 0.1851 and 0.1866β for the 1-4, 1-5 and 1-8 diols, respectively. A naive consideration will give larger extra delocalization energy for greater charge migration. Actually, if we plot these values against the magnitudes of the charge migrations from the hydroxy

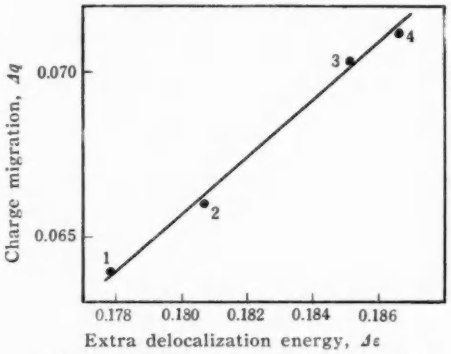


Fig. 3. Relation between the extra delocalization energy of diols and the charge migration in them.
1. phenol
2. 1-4 naphthalenediol
3. 1-5 naphthalenediol
4. 1-8 naphthalenediol

10) C. J. P. Spruit, *Rec. trav. chim.*, **68**, 309 (1949).
11) F. A. Hochstein et al., *J. Am. Chem. Soc.*, **75**, 5457 (1953).

group into the naphthalene ring, a linear relationship is obtained as shown in Fig. 3. It is surprising that a point corresponding to the phenol, which is obtained from our previous paper[9], is also located on this line. This fact gives us an interesting suggestion that the degree of charge migration will be estimated by only the calculation of orbital energies of the molecule. This seems to give a theoretical background to a well-known conception of the electronic theory in organic chemistry that the acidity of the aromatic hydroxy derivatives is closely connected with the magnitude of charge migration. In the case of α-naphthol, the value of extra-delocalization energy is $0.1862\,\beta$. Its magnitude of charge density at the hydroxy group will be, therefore, expected to be comparable with that of 1–8 diol.

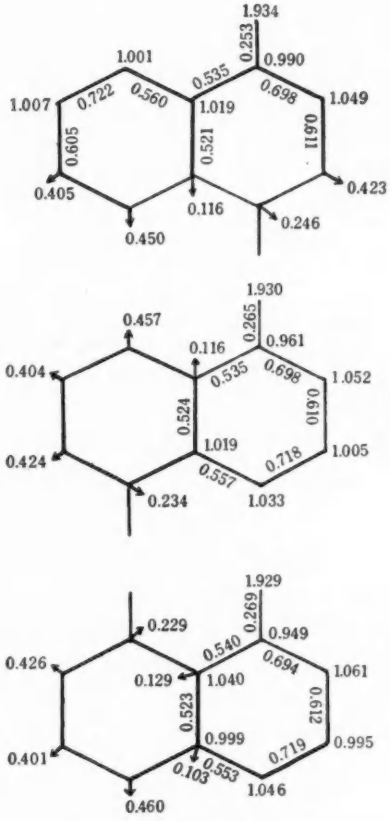


Fig. 4. Molecular diagram.

As seen from the molecular diagrams given in Fig. 4 the charge distributions in the molecules show a sharp difference according to the type of substitution, either two hydroxy groups bonded with the same ring or not. Namely, in the case of 1–4 diol the migrated charges are, for the most part, localized within one ring whereas in those of 1–5 and 1–8 diols they are equally distributed into both rings. In the discussion of the molecular properties, such as reactivity, of the naphthalene di-derivatives this characteristic charge distribution will supply a useful information.

Summary

The simple LCAO MO method was applied to the electronic structures of α,α'-naphthalenediols, using the same parameters as those of phenol based on the ASPMO calculation. The theory proved that

(a) the lowest π-orbital of the molecule would be the most sensitive to the influence of the external molecular field,

(b) the absorption spectra of diols were satisfactorily correlated with their energy level diagrams, and

(c) the extra delocalization energies produced by the charge migrations from the hydroxy groups into the naphthalene ring increased linearly with the increment of the magnitude of charge migrations.

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Expansion Formulae of Secular Determinant in Simple LCAO MO Treatment of Aromatic Hydrocarbons

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In the LCAO MO treatment of conjugated molecules, it goes without saying that the secular determinant must be known in its expanded form in order to solve it numerically. The use of secular determinant is not necessarily restricted to finding its roots. Coulson and Longuet-Higgins[1] obtained the integral formulae for electronic energy, bond order and various kinds of polarizability in which the integrands were expressed in terms of secular determinants. Also Baba[2] and the present authors[3] pointed out the importance of the coefficients in the expansion of minors of secular determinant for predicting the reactivity of alternant hydrocarbons.

In this paper, we derive several formulae which are useful for expanding the secular determinant of aromatic hydrocarbons. By using these formulae, the secular determinant can be expressed in terms of that of a smaller molecule and the laborious calculation for large molecules can be considerably simplified.

The Expansion Formulae of Secular Determinant for the Aromatic Hydrocarbon.—In the first, the types of "growth" of aromatic hydrocarbons are classified into five as shown in Fig. 1. The first, the third, and the fifth are tentatively named "even growth", and the second, and the fourth "odd growth". Then, an even molecule is formed either by an even growth of an even molecule, or otherwise by an odd growth of an odd molecule, and the formation of an odd molecule results from an odd growth of an even molecule or from an even growth of an odd molecule.

If we put the secular determinants of a molecule before and after the growth as $\Delta(\lambda)$ and $D(\lambda)$, respectively, the expansion formulae for each type are obtained as follows:

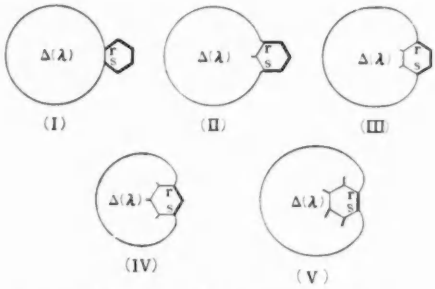

Fig. 1. The types of "growth" of aromatic hydrocarbons are shown. (I) is the first type of growth and (II) is the second type of growth and so on. The thick lines indicate the bonds formed as a result of "growth".

For the first type of growth,

$$D(\lambda)=(\lambda^4-3\lambda^2+1)\Delta(\lambda)+\lambda(\lambda^2-2)\{\Delta_{rr}(\lambda)+\Delta_{ss}(\lambda)\}+(\lambda^2-1)\Delta_{rrss}(\lambda)-2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (1)$$

For the second type of growth,

$$D(\lambda)=-\lambda(\lambda^2-2)\Delta(\lambda)-(\lambda^2-1)\{\Delta_{rr}(\lambda)+\Delta_{ss}(\lambda)\}-\lambda\Delta_{rrss}(\lambda)+2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (2)$$

For the third type of growth,

$$D(\lambda)=(\lambda^2-1)\Delta(\lambda)+\lambda\{\Delta_{rr}(\lambda)+\Delta_{ss}(\lambda)\}+\Delta_{rrss}(\lambda)-2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (3)$$

For the fourth type of growth,

$$D(\lambda)=-\lambda\Delta(\lambda)-\Delta_{rr}(\lambda)-\Delta_{ss}(\lambda)+2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (4)$$

For the fifth type of growth,

$$D(\lambda)=\Delta(\lambda)-\Delta_{rrss}(\lambda)-2(-1)^{r+s+1}\Delta_{rs}(\lambda) \quad (5)$$

Besides the above types of nuclear growth, the types of branching and bridging also exist in conjugated systems.

1) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).
2) H. Baba, This Bulletin, **30**, 147 (1957).
3) K. Fukui, T. Yonezawa, and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957).

They are shown in Fig. 2 and are tentatively designated as type 1, 2, ····· , 9. The expansion formulae for them are given as:

For the type 1,

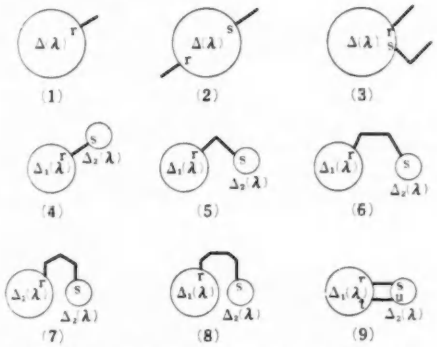

Fig. 2. The types of branching and bridging in conjugated molecules are shown. The thick lines indicate the branches {(1), (2) and (3)} and bridges {(4), (5), (6)·····, (9)} respectively.

$$D(\lambda) = -\lambda\Delta(\lambda) - \Delta_{rr}(\lambda) \tag{6}$$

For the type 2,

$$D(\lambda) = \lambda^2\Delta(\lambda) + \lambda\{\Delta_{rr}(\lambda) + \Delta_{ss}(\lambda)\} + \Delta_{rrss}(\lambda) \tag{7}$$

For the type 3,

$$D(\lambda) = (\lambda^2-1)\{-\lambda\Delta(\lambda) - \Delta_{rr}(\lambda)\} - \lambda^2\Delta_{ss}(\lambda) - \lambda\Delta_{rrss}(\lambda) \tag{8}$$

For the type 4,

$$D(\lambda) = \Delta_1(\lambda)\Delta_2(\lambda) - \Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{9}$$

For the type 5,

$$D(\lambda) = -\lambda\Delta_1(\lambda)\Delta_2(\lambda) - \Delta_{1rr}(\lambda)\Delta_2(\lambda) - \Delta_{2ss}(\lambda)\Delta_1(\lambda) \tag{10}$$

For the type 6,

$$D(\lambda) = (\lambda^2-1)\Delta_1(\lambda)\Delta_2(\lambda) + \lambda\{\Delta_{1rr}(\lambda)\Delta_2(\lambda) + \Delta_{2ss}(\lambda)\Delta_1(\lambda)\} + \Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{11}$$

For the type 7,

$$D(\lambda) = -\lambda(\lambda^2-2)\Delta_1(\lambda)\Delta_2(\lambda) - (\lambda^2-1)\{\Delta_{1rr}(\lambda)\Delta_2(\lambda) + \Delta_{2ss}(\lambda)\Delta_1(\lambda)\} - \lambda\Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{12}$$

For the type 8,

$$D(\lambda) = (\lambda^4-3\lambda^2+1)\Delta_1(\lambda)\Delta_2(\lambda) + \lambda(\lambda^2-2) \times\{\Delta_{1rr}(\lambda)\Delta_2(\lambda) + \Delta_{2ss}(\lambda)\Delta_1(\lambda)\} + (\lambda^2-1)\Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) \tag{13}$$

For the type 9,

$$D(\lambda) = \Delta_1(\lambda)\Delta_2(\lambda) - \Delta_{1rr}(\lambda)\Delta_{2ss}(\lambda) - \Delta_{1tt}(\lambda)\Delta_{2uu}(\lambda) + \Delta_{1rrtt}(\lambda)\Delta_{2ssuu}(\lambda) - 2(-1)^{r+t+1}\Delta_{1rt}(\lambda)(-1)^{s+u+1}\Delta_{2su}(\lambda) \tag{14}$$

where $\Delta(\lambda)$, $\Delta_1(\lambda)$ and $\Delta_2(\lambda)$ may be secular determinants of any conjugated system. $\Delta_{rr}(\lambda)$, or $\Delta_{ss}(\lambda)$ is the (r, r), or the (s, s) minor and $\Delta_{rrss}(\lambda)$ is the (rs, rs) minor of $\Delta(\lambda)$, and these are obtained by striking off the indicated rows and columns of $\Delta(\lambda)$. The equation of $\Delta_{rs}(\lambda)$ can be obtained according to the theorem proposed by Coulson and Longuet-Higgins[1].

The expansion formulae derived above, are very useful for obtaining secular equations of conjugated molecules, especially of large molecules.

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Density Matrix in Simple LCAO MO Method

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The LCAO MO method has been applied extensively to the explanation of the facts in organic chemical reaction. That is to say, the static method by Coulson and Longuet-Higgins[1], the localization method by Wheland[2] and the frontier electron method by Fukui et al.[3-7] and many other similar methods have been used successfully to explain the reactivity of a number of conjugated molecules.

In this article, the present authors indicate that the theoretical indexes such as electron density, bond order, and various polarizabilities derived by Coulson and Longuet-Higgins[1], can be given also by a novel method which is entirely different from that of the previous authors.

Partial Density Matrix and Hamiltonian Matrix. — First, we define the following two matrices which are most fundamental in the theory. They are referred to as partial density matrix $\mathbf{D}_j$ and Hamiltonian matrix $\boldsymbol{\alpha}$, and are defined respectively as follows:

$$\mathbf{D}_j \equiv \begin{pmatrix} (C_1^j)^2 & C_1^j C_2^j & \cdots\cdots & C_1^j C_n^j \\ C_2^j C_1^j & (C_2^j)^2 & \cdots\cdots & C_2^j C_n^j \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ C_n^j C_1^j & C_n^j C_2^j & \cdots\cdots & (C_n^j)^2 \end{pmatrix} \tag{1}$$

$$\boldsymbol{\alpha} \equiv \begin{pmatrix} \alpha_1 & \beta_{12} & \cdots\cdots & \beta_{1n} \\ \beta_{21} & \alpha_2 & \cdots\cdots & \beta_{2n} \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \beta_{n1} & \beta_{n2} & \cdots\cdots & \alpha_n \end{pmatrix} \tag{2}$$

$$(\beta_{rs} = \beta_{sr})$$

where C_r^j is the coefficient of atomic orbital, ϕ_r, in molecular orbital ψ_j, that is, according to the usual LCAO MO method, ψ_j is expressed as a linear combination of atomic orbitals whose number is n; $\psi_j = \sum_{r=1}^{n} C_r^j \phi_r$. α and β are the Coulomb and the resonance integral, respectively. From Eqs. 1 and 2 the following formulae are easily obtained:

$$\boldsymbol{\alpha}\mathbf{D}_j = \varepsilon_j \mathbf{D}_j \tag{3}$$

$$\boldsymbol{\alpha}\mathbf{D}_j = \mathbf{D}_j \boldsymbol{\alpha} \tag{4}$$

The partial density matrices have the following relations with each other;

$$\mathbf{D}_j = \mathbf{D}_j^2 = \mathbf{D}_j^3 = \cdots\cdots \tag{5}$$

$$\mathbf{D}_j \mathbf{D}_k = 0 \quad (j \neq k) \tag{6}$$

$$\mathbf{D}_j = \frac{\mathbf{D}_j \boldsymbol{\alpha} \mathbf{D}_j}{\varepsilon_j} \tag{7}$$

$$\mathbf{D}_k \boldsymbol{\alpha} \mathbf{D}_j = 0 \quad (k \neq j) \tag{8}$$

$$\sum_{j=1}^{n} \mathbf{D}_j = \mathbf{E} \tag{9}$$

where $\mathbf{E}$ is unit matrix.

Variation of $\mathbf{D}_j$ leads us to the following relations,

$$\mathbf{D}_j \cdot \delta\mathbf{D}_j + \delta\mathbf{D}_j \cdot \mathbf{D}_j = \delta\mathbf{D}_j \tag{10}$$

$$\mathbf{D}_j \cdot \delta\mathbf{D}_k + \delta\mathbf{D}_j \cdot \mathbf{D}_k = 0 \quad (k \neq j) \tag{11}$$

$$\mathbf{D}_j \cdot \delta\mathbf{D}_j \cdot \mathbf{D}_j = 0 \tag{12}$$

$$\mathbf{D}_k \cdot \delta\mathbf{D}_j \cdot \mathbf{D}_k = 0 \quad (k \neq j) \tag{13}$$

$$\mathbf{D}_k \cdot \delta\mathbf{D}_j \cdot \mathbf{D}_l = 0 \quad (l \neq j,\ k \neq j) \tag{14}$$

Perturbation Theory in Density Matrix. — The perturbation theory in density matrix can be constructed in just the same way as in LCAO MO method. When the Hamiltonian matrix $\boldsymbol{\alpha}$ is subjected to perturbation by the amount of $\delta\boldsymbol{\alpha}$, $\mathbf{D}_j$ and ε_j are assumed to become $\mathbf{D}_j + \delta\mathbf{D}_j$ and $\varepsilon_j + \delta\varepsilon_j$, respectively. Then from Eq. 3, the following formulae are obtained.

$$\mathbf{D}_j \cdot \delta\varepsilon_j = \delta\boldsymbol{\alpha} \cdot \mathbf{D}_j + (\boldsymbol{\alpha} - \varepsilon_j)\delta\mathbf{D}_j \tag{15}$$

Multiplying Eq. 15 by $\mathbf{D}_k$ $(k \neq j)$ from the left-hand side, we gain the following relation,

1) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).
2) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
3) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).
4) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954).
5) K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954).
6) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957).
7) K. Fukui, T. Yonezawa and C. Nagata, ibid., **27** 1247 (1957).

$$\mathbf{D}_k\cdot\delta\mathbf{D}_j=\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{16}$$

Similarly, from Eqs. 11 and 16,

$$\delta\mathbf{D}_j\cdot\mathbf{D}_k=\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k} \tag{17}$$

From Eqs. 16 and 17, using the idempotent nature of $\mathbf{D}_j$ we easily obtain the following formulae:

$$\mathbf{D}_k\cdot\delta\mathbf{D}_j\cdot\mathbf{D}_j=\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k}\quad(k\neq j) \tag{18}$$

$$\mathbf{D}_j\cdot\delta\mathbf{D}_j\cdot\mathbf{D}_k=\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k}\quad(k\neq j) \tag{19}$$

From Eqs. 9, 16 and 17,

$$(\mathbf{E}-\mathbf{D}_j)\delta\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{20}$$

$$\delta\mathbf{D}_j(\mathbf{E}-\mathbf{D}_j)=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k} \tag{21}$$

are obtained. These formulae can be transformed to the following formulae by the aid of Eq. 10, that is

$$\delta\mathbf{D}_j\cdot\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{22}$$

$$\mathbf{D}_j\cdot\delta\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k}{\varepsilon_j-\varepsilon_k} \tag{23}$$

After adding Eqs. 22 and 23, we use the relation in Eq. 10, then $\delta\mathbf{D}_j$ is expressed as

$$\delta\mathbf{D}_j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k+\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{24}$$

If Eq. 15 is multiplied by $\mathbf{D}_j$ from the left-hand side, the following equation is obtained, that is

$$\mathbf{D}_j\cdot\delta\varepsilon_j=\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j \tag{25}$$

Taking the (r, r) element of Eq. 24, we obtain

$$\delta C_r^j=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{C_r^k\sum_t\sum_u C_t^jC_u^k(\delta\boldsymbol{\alpha})_{tu}}{\varepsilon_j-\varepsilon_k} \tag{26}$$

Similarly, the (r, r) element of Eq. 25 becomes

$$\delta\varepsilon_j=\sum_t\sum_u C_t^jC_u^j(\delta\boldsymbol{\alpha})_{tu} \tag{27}$$

Now, we define the density matrix $\mathbf{Q}$ as the sum of the partial density matrices, namely,

$$\mathbf{Q}=\sum_{j=1}^{n}\nu_j\mathbf{D}_j=\begin{pmatrix}q_1 & p_{12} & \cdots & p_{1n}\\ p_{21} & q_2 & \cdots & p_{2n}\\ \cdots & \cdots & \cdots & \cdots\\ \cdots & \cdots & \cdots & \cdots\\ p_{n1} & p_{n2} & \cdots & q_n\end{pmatrix} \tag{28}$$

where q and p stand for the electron density and the bond order defined by Coulson and Longuet-Higgins and ν_j is the number of electrons in the jth molecular orbital. Then the variation of density matrix is written as

$$\delta\mathbf{Q}=\sum_{j=1}^{n}\nu_j\delta\mathbf{D}_j=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{\mathbf{D}_j\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_k+\mathbf{D}_k\cdot\delta\boldsymbol{\alpha}\cdot\mathbf{D}_j}{\varepsilon_j-\varepsilon_k} \tag{29}$$

If we take the (r, r) and the (r, s) elements of Eq. 29, δq_r and δp_{rs} are obtained respectively.

$$\delta q_r=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{2C_r^jC_r^k\sum_t\sum_u C_t^jC_u^k(\delta\boldsymbol{\alpha})_{tu}}{\varepsilon_j-\varepsilon_k} \tag{30}$$

$$\delta p_{rs}=\sum_{j=1}^{n}\nu_j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{(C_r^jC_s^k+C_s^jC_r^k)\sum_t\sum_u C_t^jC_u^k(\delta\boldsymbol{\alpha})_{tu}}{\varepsilon_j-\varepsilon_k} \tag{31}$$

The total π-electron energy E is the sum of the orbital energy ε_j, that is

$$E=\sum_{j=1}^{n}\nu_j\varepsilon_j \tag{32}$$

then, from Eq. 27, is expressed as

$$\delta E=\sum_{j=1}^{n}\nu_j\delta\varepsilon_j=\sum_{j=1}^{n}\nu_j\sum_t\sum_u C_t^jC_u^j(\delta\boldsymbol{\alpha})_{tu} \tag{33}$$

Relations among Theoretical Indexes.—Differentiating $\delta\varepsilon_j$, δE, and δC_r^j with respect to α and β, we obtain the following relations:

$$\frac{\partial\varepsilon_j}{\partial\alpha_r}=(C_r^j)^2 \tag{34}$$

$$\frac{\partial\varepsilon_j}{\partial\beta_{rs}}=2C_r^jC_s^j \tag{35}$$

$$\frac{\partial E}{\partial\alpha_s}=\sum_{j=1}^{n}\nu_j(C_r^j)^2=q_r \tag{36}$$

$$\frac{\partial E}{\partial\beta_{rs}}=2\sum_{j=1}^{n}\nu_jC_r^jC_s^j=2p_{rs} \tag{37}$$

$$\frac{\partial C_r^j}{\partial\alpha_s}=C_s^j\sum_{\substack{k=1\\k\neq j}}^{n}\frac{C_r^kC_s^k}{\varepsilon_j-\varepsilon_k} \tag{38}$$

$$\frac{\partial C_r^j}{\partial\beta_{st}}=\sum_{\substack{k=1\\k\neq j}}^{n}\frac{C_r^k(C_s^jC_t^k+C_t^jC_s^k)}{\varepsilon_j-\varepsilon_k} \tag{39}$$

These equations coincide with those

derived by Coulson and Longuet-Higgins[1]. Similarly, from Eqs. 30 and 31, the following formulae are obtained and these are nothing but the polarizabilities defined by Coulson and Longuet-Higgins[1].

$$\frac{\partial q_r}{\partial \alpha_s} = \sum_{j=1}^{n} \nu_j \sum_{\substack{k=1 \\ k \neq j}}^{n} \frac{2C_r^j C_r^k C_s^j C_s^k}{\varepsilon_j - \varepsilon_k} \tag{40}$$

$$\frac{\partial q_r}{\partial \beta_{st}} = \sum_{j=1}^{n} \nu_j \sum_{\substack{k=1 \\ k \neq j}}^{n} \frac{2C_r^j C_r^k (C_s^j C_t^k + C_t^j C_s^k)}{\varepsilon_j - \varepsilon_k} \tag{41}$$

$$\frac{\partial p_{rs}}{\partial \alpha_t} = \sum_{j=1}^{n} \nu_j \sum_{\substack{k=1 \\ k \neq j}}^{n} \frac{C_t^j C_t^k (C_r^j C_s^k + C_s^j C_r^k)}{\varepsilon_j - \varepsilon_k} \tag{42}$$

$$\frac{\partial p_{rs}}{\partial \beta_{tu}} = \sum_{j=1}^{n} \nu_j \sum_{\substack{k=1 \\ k \neq j}}^{n} \frac{(C_r^j C_s^k + C_s^j C_r^k)(C_t^j C_u^k + C_u^j C_t^k)}{\varepsilon_j - \varepsilon_k} \tag{43}$$

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Rapid Colorimetric Determination of Selenium by the Tin(II)-Strong Phosphoric Acid Reduction Method

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With the increasing demand of the electronic industry for selenium, the element has become critically important, and a rapid and accurate method of detecting and determining the element is badly wanted in the field and in the laboratory. Although selenium occurs widely in many geological formations frequently accompanied with minerals containing sulfur, the amount is so small that chemical analysis of the element is one of the most difficult of techniques. The procedures which have been presented by most investigators are of two parts: decomposition of samples with oxidizing acids, and estimation of the selenium in the solution. However, it is really regrettable that in all the methods the decomposition of the samples is time-consuming and loss of the element is likely to occur during the evaporation of the solution or filtration of the undissolved residue.

Previously the authors devised a new powerful decomposing and reducing agent, tin(II)-strong phosphoric acid[1], by which sulfur in inorganic substances such as ores[2] as well as in organic compounds[3,4] could be taken out as hydrogen sulfide and readily estimated iodimetrically or colorimetrically. A further attempt was made by the present authors to reduce selenates, selenites, and elementary selenium to hydrogen selenide by treatment with the same reagent. As the result of the preliminary experiments it was found that selenium in various forms could be reduced to hydrogen selenide at somewhat higher temperatures than in the case of sulfur. By the powerful decomposing power of the reagent even pyrite can readily and completely be decomposed without any other treatment, and the selenium can be separated as gaseous hydrogen selenide from the sample. The present paper describes the investigation by which a new method for quantitative analysis of selenium is established.

1) T. Kiba et al., This Bulletin, **28**, 641 (1955).
2) T. Kiba, I. Akaza and N. Sugishita, ibid., **30**, 972 (1957).
3) S. Ohashi, ibid., **28**, 645 (1955).
4) T. Kiba, I. Akaza and S. Taki, ibid., **30** 482 (1957).

Experimental

Apparatus —The apparatus used in this study is shown in Fig. 1. It is composed of two parts, a reaction vessel (A) and an absorbing part (B). The reaction vessel (A) is a round-bottomed flask of hard glass having a glass cap fitted to its top and provided with inlet and outlet tubes for hydrogen gas. The absorbing part (B) is composed of two test-tubes 3 cm. in diameter. A gas delivery tube (G) is connected with a piece of rubber tubing (R) to the outlet arm of the reaction vessel (A) and inserted into the absorbing solution. A Kipp's apparatus is employed for the production of hydrogen, which is purified by four gas-washing bottles (not shown in the figure) and introduced in the reaction vessel

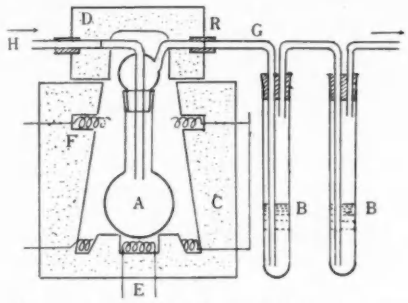

Fig. 1. Apparatus for reduction of selenium and absorption of hydrogen selenide.
A: Reaction vessel, a round-bottomed flask
B: Absorbing vessels
C: Block of diatomaceous earth
D: Cover block of diatomaceous earth
E: Electric heater at the bottom
F: Electric heater around the sides
G: Gas-delivery tube
H: Hydrogen gas introduced into A
R: Short piece of rubber tubing

through the inlet arm. The solution used for the purification of hydrogen is described below.

Reagents. — *Strong phosphoric acid.* — Four hundred grams of commercial orthophosphoric acid of extra pure grade (d=1.7) is placed in a 300 ml. conical beaker, and dehydrated by heating on a 500 W hot plate until a thermometer dipped in the liquid indicates 300°C. If the heating takes too long the liquid will become turbid and viscous and useless for the purpose in view. During the heating, the water vapor and the mist of phosphoric acid coming off should be rapidly removed from the neighborhood of the liquid surface through a glass tube, one end of which is held near the liquid surface, the other end being connected to a suction pump. It saves much time in the dehydration.

Tin(II)-strong phosphoric acid.—Fifty grams of tin(II)-chloride dihydrate of extra pure grade is placed in a 300 ml. conical beaker and on it is poured 250 g. of the strong phosphoric acid prepared as described above. The content is heated to 300°C within about 30 min. in the manner of preparation of strong phosphoric acid. After cooling, the tin(II)-strong phosphoric acid thus obtained, a very viscous and possibly slightly turbid liquid, may be stored in a closed vessel.

Tin(II)-chloride solution.—15% in 9N hydrochloric acid.

Gum arabic solution.—1% aqueous solution.

Hydrogen gas.—Hydrogen gas produced in the Kipp's apparatus is purified by passing through four gas washing bottles containing respectively, water, 1% potassium permanganate in 10% sodium carbonate solution, 2% vanadium(II) sulfate in 6N sulfuric acid solution, and 5% barium chloride, and is introduced into the reaction vessel through a glass tube in which a copper net is placed to prevent accidental explosion of the gas.

Standard selenious acid solution. — Elementary selenium is dissolved in concentrated nitric acid and evaporated to dryness, and the selenious acid thus formed is sublimed by gentle heating in another vessel. The sublimate is collected and dissolved in water to make a solution containing 3 mg. of selenium in 1 ml. The solution is diluted to a suitable concentration for the following experiments.

Pyrite ore. — Natural pyrite from the Ogoya Mine near Kanazawa City was ground to 200 mesh size and used as a sample to test the procedure established by the present authors.

Other reagents were all of the pure chemical grade and the utensils were of the ordinary kind for the laboratory.

Procedure.—(1) *Decomposition of samples and evolution of hydrogen selenide.*—Take an accurately measured sample—pipet a solution; weigh a solid—containing selenium and put it into the reaction vessel (A, in Fig. 1). The volume of the vessel should be varied according to the amount of the sample to be analyzed. Evaporate to dryness if the sample is a solution. Pour about 10 to 50 g. of tin(II)-strong phosphoric acid over the sample. Put 5 to 10 ml. of 5N sodium hydroxide solution into each of the absorbing apparatuses as shown in Fig. 1. Connect all the apparatuses. Pass hydrogen gas very rapidly through the apparatus for five minutes to expel the air from the apparatus. Then reduce the flow of the gas to rate of one bubble per second. Cover the top of the reaction vessel with a block of diatomaceous earth (D) as shown in Fig. 1. Heat the bottom and the sides of the reaction vessel by passing an electric current through nichrome wires placed in the diatomaceous earth blocks (C). The voltage of the current should be regulated by a variable transformer. It is unnecessary to keep the reaction temperature constant, but it should be high enough that the content of the reaction vessel seems to be solidified when cooled after the reaction. After about twenty or thirty minutes the heating is stopped.

Disconnect the absorbing vessels from the gas-outlet arm of the reaction vessel, and transfer the contentin to a 100 ml. Erlenmeyer flask with sufficient washings of the gas-delivery tube. Add 30% hydrogen peroxide solution carefully, drop by drop, since when a relatively large amount of sulfur is present the oxidation takes place explosively. By the above treatment hydrogen selenide is oxidized to selenic acid, and hydrogen sulfide to sulfuric acid. Boil the solution for about ten minutes to decompose the residual hydrogen peroxide completely, and cool the solution by dipping the vessel in running water. Add enough concentrated hydrochloric acid to neutralize the sodium hydroxide and 20 ml. in excess to the solution. Boil the contents for about twenty minutes

with a reflux. By this treatment the selenic acid is reduced to selenious acid, whereas the sulfuric acid remains unchanged.

(2) *Photometric determination of selenium.*—Transfer the content of the flask into a 100 ml. measuring flask, put 4 ml. of gum arabic solution in it, and add water to make the total volume about 95 ml. Place the vessel in a thermostat kept at 45°C, and when the temperature of the liquid has become constant, add 5 ml. of the tin(II) chloride solution and leave the vessel in the thermostat for about twenty minutes. Then, the selenious acid will have been reduced to colloidal elementary selenium having a red color. Add more water till the liquid level comes to the mark, and measure the absorbancy of the solution with a photoelectric colorimeter using a 372 mμ-filter and 10 mm.-cells.

A working curve for the colorimetric measurement should be prepared by carrying out the same procedure with known amounts of selenious acid.

Results and Discussion

Reduction of Selenious Acid by the Tin(II)-Strong Phosphoric Acid.—A definite volume of the standard selenious acid solution was placed in the reaction vessel and the reduction of the acid and the evolution of hydrogen selenide were carried out by the procedure. The recovery of the selenium is satisfactory as shown in Table I, 0.1 to 2.5 mg. of selenium being recovered with relative deviation not exceeding 5%.

TABLE I. RECOVERY OF SELENIUM BY THE METHOD

Se Taken[a]	Number of Experiment	Se Found (Average) mg.	Standard Deviation
0.094	4	0.096	0.004_5
0.305	4	0.308	0.012_3
0.471	4	0.465	0.001_7
1.016	4	0.99	0.05_4
1.52	4	1.48	0.03_6
2.03	4	2.04	0.06_7
2.54	4	2.54	0.05_0

a) Selenium was taken as selenious acid.

TABLE II. RECOVERY OF SELENIUM IN PRESENCE OF SULFUR

Na_2SO_4 Taken g.	Se Taken mg.	Se Found mg.	Recovery of Se %
0.2	0.102	0.103	100.9
0.3	0.305	0.314	102.9
0.2	0.508	0.508	100.0
0.2	1.02	1.00	98.0
0.2	1.52	1.48	97.4
0.2	2.03	1.98	97.5
0.2	2.54	2.47	97.3
0.8	0.508	0.508	100.0

Determination of Selenium in Presence of Sulfur.—As selenium is often accompanied with a larger amount of sulfur, it was deemed necessary that the effect of sulfur on this method be first examined. A mixed solution of sodium sulfate and sodium selenite in various ratios was employed for the test, and the determination of the selenium was done according to the procedure described above. The results are shown in Table II, from which it is confirmed that the presence of forty to two hundred parts of sulfur for one part of selenium does not interfere with the determination of the latter. When still larger amounts of sulfur are present in the sample, larger amounts of the tin(II)-strong phosphoric acid should be employed to decompose the sample and to remove the sulfur as hydrogen sulfide. In such cases, a larger amount of the absorbing solution of sodium hydroxide should be used.

Determination of Selenium in Presence of Sulfur and Iron.—Before the method is applied to the determination of selenium in a sulfur-containing ore such as pyrite, the effect of iron should be first examined by carrying out the procedure with a synthetic sample. The analysis was performed with a mixed solution of iron(III) sulfate and sodium selenite for this purpose. As shown in Table III, iron has no influence on the determination of selenium. So the procedure presented above may safely be applied to the determination of selenium in pyrite.

TABLE III. RECOVERY OF SELENIUM IN PRESENCE OF IRON(III) SULFATE

$Fe_2(SO_4)_3$ Taken	Se Taken mg.	Se Found mg.
0.4	0.102	0.102
0.4	2.54	2.54
0.4	0.508	0.504

Determination of Selenium in Pyrite.—As all the sulfur and the selenium in the ore could be removed as hydrogen sulfide and hydrogen selenide, respectively, all troublesome treatments such as the dissolving of the ore in nitric and hydrochloric acids and the evaporation of the solution were dispensed with by a single treatment with the tin(II)-strong phosphoric acid. The results obtained by this method are tabulated in Table IV, which are in good agreement with the results obtained by the ordinary acid-dissolving

TABLE IV. ANALYSIS OF SELENIUM IN PYRITE

(a) TIN(II)-STRONG PHOSPHORIC ACID REDUCTION METHOD

Pyrite Taken g.	Se Found mg.	Se Found p.p.m.
1.24	0.111	89
1.03	0.093	90
2.05	0.187	91
2.01	0.178	89
3.02	0.271	90
2.99	0.258	86

(b) HYDROCHLORIC-NITRIC ACID DECOMPOSITION METHOD

Pyrite Taken g.	Se Found mg.	Se Found p.p.m.
10.0	0.843	84
10.0	0.860	86
10.0	0.868	87

method. This method takes about two hours, while the usual method takes five or more hours.

Color System of Selenium. — Many methods have been described for the colorimetric determination of minute amounts of selenium, e.g., coloration of elementary selenium by reduction with tin(II) chloride or other reducing agents[5], colorization by pyrrol[6], and by diaminobenzidine[7], but the tin(II) chloride method is considered the simplest. So the method was preferred in this study. To determine the optimum operating wavelength for absorption spectrometry of selenium, an absorbancy-wavelength curve was plotted by means of a spectrophotometer (Hitachi Ltd., Model EPU-2). covering the range between 320 and 500 mμ. The conditions of the experiment were the same as those described in the procedure, The curves obtained are shown in Fig. 2, in which it is seen that remarkable absorption takes place in the ultraviolet region, but the absorbancy of the blank, the solution containing no selenium, increases also in the same region. The authors chose 372 mμ as the optimum wavelength, at which the absorbancy of the blank is scarcely perceptible, and the absorbancy obeys Beer's law when the selenium concentration is from 0.1 to 0.25 mg. in 100 ml. The relation between the amount of the selenium taken and the absorbancy measured is expressed by the following equation which was computed from twenty-five measurements by the method of least squares

$$x = 3.558\,I$$

where, x is the amount of selenium taken and I the absorbancy measured. A working curve involves a standard deviation of about 1.5%.

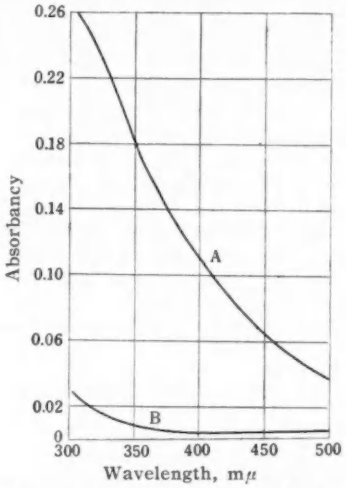

Fig. 2. Spectral absorbance of colloidal selenium.
A: A solution containing 0.6 mg. of selenium, 3 ml. of 15% tin(II) chloride in 9 N hydrochloric acid, and 10 ml. of concentrated hydrochloric acid in 100 ml.
B: The same solution without the selenium.

Summary

A new procedure for a rapid determination of selenium has been devised by the present authors. Tin(II)-strong phosphoric acid, previously prepared by the authors, has a remarkable decomposing and reducing power, and selenium in various forms can be reduced to hydrogen selenide which is evolved as a gas from samples. Sulfur in various forms is reduced to hydrogen sulfide at the same time. Solid samples such as pyrite can be allowed to decompose rapidly by simple heating with the reagent in an atmosphere of hydrogen. The gas evolved is introduced into an absorbing solution of 5 N sodium hydroxide. Then, a small

5) J. Fidler, *Chem. Listy*, **46**, 221 (1952).
6) S. Hirano, M. Suzuki and T. Noguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **55**, 514 (1952).
7) K. L. Cheng, *Anal. Chem.*, **28**, 1738 (1956).
8) H. Goto et al., *Sci. Repts. Research Inst. Tohoku Univ.*, **A, 4**, 28 (1952); **4**, 121 (1952); **5**, 34 (1953); **7**, 23 (1955).

volume of 30% hydrogen peroxide solution is added. Thus sodium selenate and sodium sulfate are formed in the solution. After adding an excess of concentrated hydrochloric acid and boiling for about twenty minutes with a reflux condenser, the selenic acid is reduced to selenious acid, while the sulfuric acid remains unchanged. The solution is kept at 45°C for several minutes, and solutions of gum arabic and tin(II) chloride are added successively. The red color of the elementary selenium is measured at 372 mμ by a photoelectric colorimeter. The recovery of selenium is uniform even in the presence of large amounts of sulfur and iron. The analysis of selenium in pyrite was carried out by this procedure, and the results were in good agreement with those obtained by other methods.

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Crystal Structure of 2-Chloro-1-aza-azulene

By Chihiro TAMURA*, Yoshio SASADA and Isamu NITTA

(Received December 2, 1958)

We have studied several crystal structures of the molecules containing a seven-membered carbon ring, such as tropolone hydrochloride, sodium tropolonate and 1-oxa-azulan-2-one[1-7]. As a part of these serial investigation, the present account deals with the crystal structure of 2-chloro-1-aza-azulene, which Professor T. Nozoe and his collaborators kindly supplied us.

Experimental

Crystal and physical data obtained are: 2-Chloro-1-aza-azulene, C_9H_6NCl, m.p. 72~73°C. Monoclinic, $a=16.00\pm0.07$, $b=7.50\pm0.04$, $c=7.03\pm0.03$ Å, $\beta=113.8\pm0.5°$C.

Absent spectra; $(h\,0\,l)$ when h is odd, $(0\,k\,0)$ when k is odd. Space group; $P2_1/a-\frac{3}{2}C_h$. Four molecules per unit cell. Volume of unit cell; 771.9 Å^3. Density (by flotation); 1.40 g.cm^{-3}. Density (calculated); 1.41 g.cm^{-3}. Linear absorption coefficient for Cu K_α radiation,

$$\mu = 37.5\,\text{cm}^{-1}$$

Total number of electrons per unit cell, $F(0\,0\,0)=336$.

Weissenberg photographs were taken at room temperature around the b and c axes, using Cu K_α radiation. The crystals used, which were cut from a large brown block, were square in cross section with rectangular dimensions:

0.05×0.06 cm. for the b axis rotation,

0.06×0.08 cm. for the c axis rotation.

Intensities were estimated by visual comparison with a calibrated scale. The multiple-film technique was used to correlate strong and weak reflexions, ranging in relative intensities from 8000 to 1 for $(h\,0\,l)$ and from 6000 to 1 for $(h\,k\,0)$ reflexions. Reflexions from 102 and 76 planes were observed out of 135 possible $(h\,0\,l)$'s and 143 $(h\,k\,0)$'s respectively. The corrections for polarization and Lorentz factors were made in the usual way, and that for absorption was omitted.

Results

Structure Determination. — The initial step was intended to locate the chlorine atom by computing Patterson functions $P(uw)$ and $P(uv)$. $P(uw)$ showed three broad peaks, of which two overlapped each other. While the possibility that the one peak is due to the interatomic vector between two chlorines can be excluded by the comparison with $P(uv)$, it was impossible to decide which of the remaining two corresponds to the actual

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1) Y. Sasada and I. Nitta, *Acta Cryst.*, **9**, 205 (1956).
2) Y. Sasada, K. Osaki and I. Nitta, ibid., **7**, 113 (1954).
3) Y. Sasada and I. Nitta, This Bulletin, **30**, 62 (1957).
4) Y. Sasada, ibid., **32**, 165 (1959).
5) Y. Sasada, ibid., **32**, 171 (1959).
6) Y. Takaki, Y. Sasada and I. Nitta, to be published.
7) K. Furukawa, Y. Sasada and T. Watanabé, to be published.

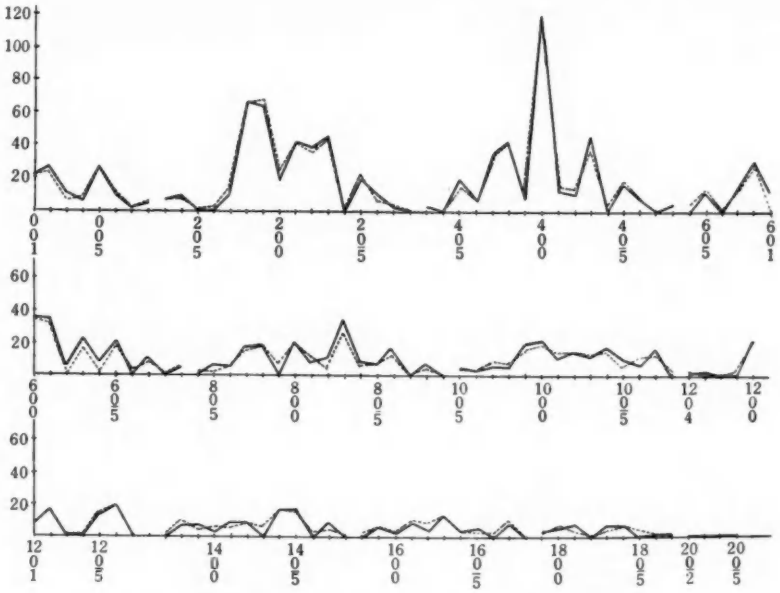

Fig. 1. Observed and calculated structure factors, $F(h\,0\,l)$.
—— $F_{obs.}$, ····· $F_{calc.}$

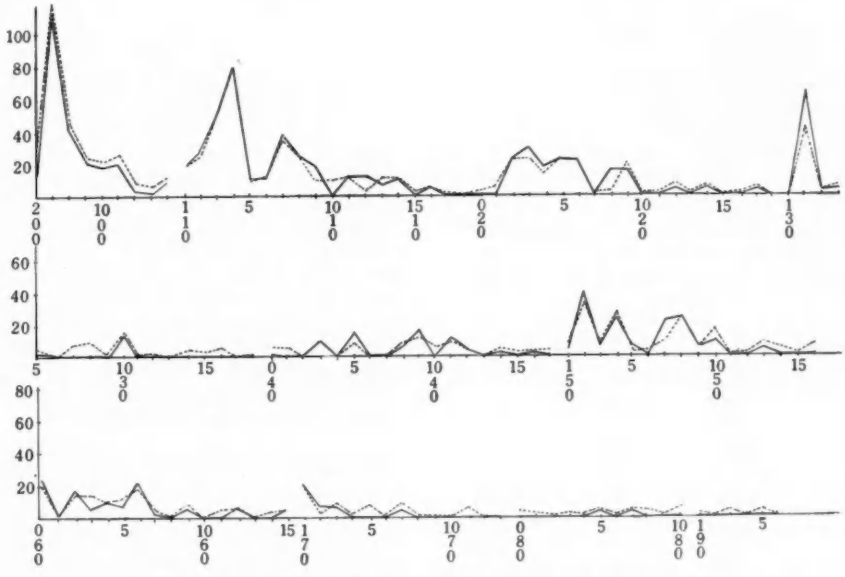

Fig. 2. Observed and calculated structure factors, $F(h\,k\,0)$.
—— $F_{obs.}$, ····· $F_{calc.}$

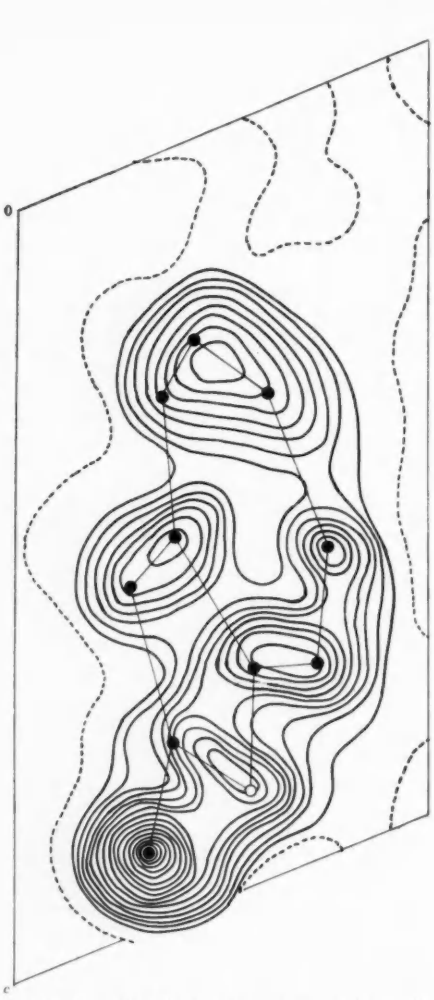

Fig. 3. The final Fourier projection of the electron density along the b axis. Contours at intervals 1 eÅ^{-2}. Contour at 1 eÅ^{-2} is broken.

TABLE I. ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Cl	0.080_5	0.064	0.903
N	0.142	0.401	0.868
C_2	0.097	0.230	0.772
C_3	0.073_5	0.227	0.546
C_4	0.090_5	0.466	0.330
C_5	0.111_5	0.622	0.264
C_6	0.152_5	0.772	0.365
C_7	0.191_5	0.798	0.603
C_8	0.187	0.657	0.758
C_9	0.147	0.494	0.715
C_{10}	0.097	0.390	0.510

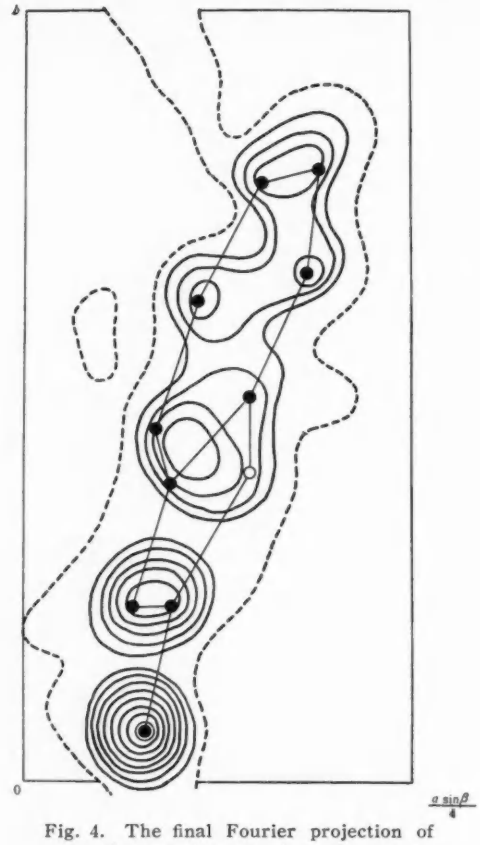

Fig. 4. The final Fourier projection of the electron density along the c axis. Contours at intervals of 2 eÅ^{-2}. Contour at 2 Å^{-2} is broken.

Cl–Cl vector. Therefore, the trial method was applied to $(h\,0\,l)$ first, in order to obtain the x and z coordinates of all atoms. After satisfactory x and z coordinates were determined, y coordinates were estimated by the trial for $(h\,k\,0)$. Refinements of these atomic coordinates were made by successive two-dimensional Fourier and the least square method. The final atomic coordinates of the chlorine, nitrogen and carbon are listed in Table I. Calculated structure factors $F(h\,0\,l)$ and $F(h\,k\,0)$ are shown with broken lines in comparison with observed values (full lines) in Figs. 1 and 2 respectively. In the structure-factor calculations the atomic scattering factors were taken from McWeeny's paper[8], the values for "valence states" being used for carbon. The best B factors were 3.5 and 4.5 Å^2 for $(h\,0\,l)$ and $(h\,k\,0)$

8) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

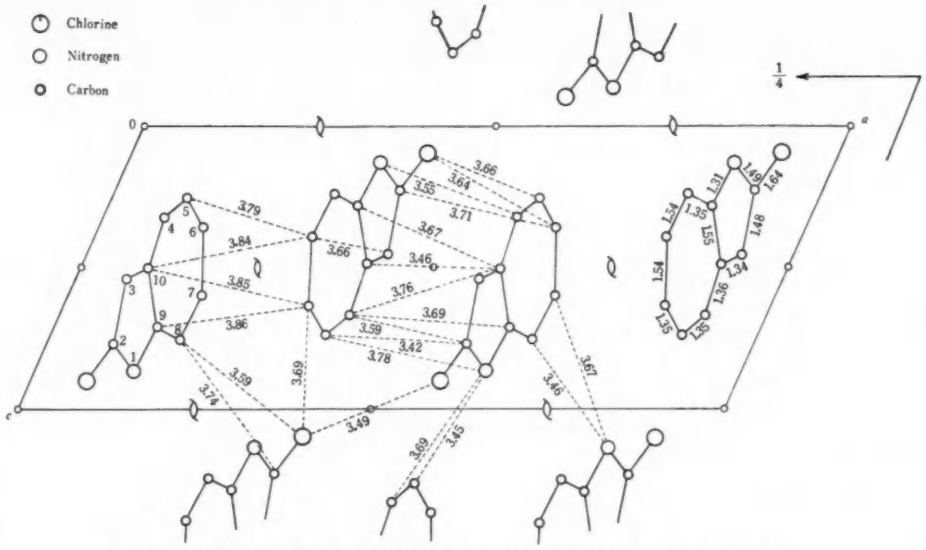

Fig. 5. Arrangement of molecules in the (010) projection, with intra- and intermolecular distances (Å).

respectively. At this stage, R indices become 0.176 for $(h\,0\,l)$ and 0.231 for $(h\,k\,0)$, if non-observed reflexions are omitted. The electron density projections along the b and c axes are shown in Figs. 3 and 4 respectively.

Description of the Structure.—As the scattering factors modified by thermal coefficients for nitrogen and carbon are hardly different, it is difficult at the earlier stage of analysis to decide which of the atoms, 1 or 3 numbered as shown in Fig. 5 corresponds to the nitrogen. If the atom at 3-position is nitrogen, the R index for $(h\,0\,l)$ becomes 0.185. On the other hand, if the atom at 1-position is nitrogen, the R index is 0.176 as described in the preceding paragraph. Moreover, the intermolecular distances show that the atom at 1-position has the near approaches to neighboring molecules such as 3.45 and 3.46 Å, which seem unreasonable for the CH–CH contacts. Thus it may be concluded that the atom at the 1-position is nitrogen.

Molecular dimensions (shown in Fig. 5) can not be discussed in detail in view of the rather large standard deviations of the coordinates.

Crystal structure projected along the b axis is shown in Fig. 5. There are no large discrepancies from the ordinarily accepted range of values for the intermolecular approaches. The long and short axes of the molecule make angles of about 50° and 30° with the (0 1 0) plane respectively. An outline of the molecular arrangement in this crystal seems to be of the intermediate type between those in azulene[9] and 1-oxa-azulan-2-one[4,5].

The authors wish to express their sincere thanks to Professor T. Nozoe for supplying the sample and for his continued interest.

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9) J. M. Robertson, H. M. M. Shearer, G. A. Sim and D. G. Watson, *Nature*, **182**, 177 (1958).

*Thermodynamic Studies on Cobalt Complexes. II. Solubility and Standard Free Energy of Formation of $[CoA_6]$-type Salts**

By Motoshichi MORI, Ryokichi TSUCHIYA and Yasuhiro OKANO

(Received August 8, 1958)

Although there are numerous investigations on the cobalt complexes, very few reports[1] have been published on the solubility of these complexes determined at different temperatures, and consequently neither the calculations of the heat of solution have been made nor the discussions from the view point of thermodynamics have been carried on.

In the present study the solubilities of hexamminecobalt(III) complexes in water were determined at various temperatures, and on the basis of these data and from the activity coefficient of hexamminecobalt(III) chloride reported in the preceding paper[2] the heat of solution and the free energy change of the solution were calculated. By using the latter and the standard free energy of formation of the hexamminecobalt(III) ion already known, the standard free energy of formation was calculated for solid hexamminecobalt(III) chloride, bromide, nitrate and perchlorate.

Experimental

Hexamminecobalt(III) chloride was prepared by Bjerrum's method[3]. Hexamminecobalt(III) bromide, nitrate and perchlorate were precipitated from the aqueous solution of the chloride by adding ammonium bromide, nitric acid and perchloric acid, respectively.

Sufficient amount of the sample and water to form the saturated solution was poured into a flask, which was dipped into the thermostat at the desired constant temperature. After the equilibrium of the solution was attained, an aliquot of the solution was taken out through asbestos by a measuring pipette and the solubility was calculated by analyzing the cobalt content of the solution by iodometry[4].

By measuring the specific gravity of the saturated solution by a hydrometer at each temperature the molality m was calculated by means of the following formula,

$$m = 1000C/(1000d - CM)$$

where C is the molar concentration, d, the specific gravity of saturated solution and M, the molecular weight of the solute.

Results

The results obtained for the hexamminecobalt(III) chloride, bromide, nitrate and perchlorate are summarized in Tables I, II, III and IV, respectively.

In the Tables I—IV, $\gamma_\pm$ is the mean activity coefficient of the complex and K is the equilibrium constant of the solution. The methods of the calculation of them are given in the following discussion.

Discussion

Hexamminecobalt(III) Chloride.—When the hexamminecobalt(III) chloride is dissolved into water the change is expressed by,

$$[Co(NH_3)_6]Cl_3(s) = [Co(NH_3)_6]Cl_3(aq.\,a)$$
$$= [Co(NH_3)_6]^{3+}(aq.) + 3Cl^-(aq.)$$

If the activities of the complex salt, the complex cation and the anion in the solution are expressed by $a_{[Co(NH_3)_6Cl_3]}$, $a_{[Co(NH_3)_6]^{3+}}$ and a_{Cl^-} respectively, and the activity coefficients of the complex cation and the anion by $\gamma_{[Co(NH_3)_6]^{3+}}$ and γ_{Cl^-}, the equilibrium constant of the solution, K, is given as follows:

$$K = a_{[Co(NH_3)_6]Cl_3} = a_{[Co(NH_3)_6]^{3+}} \cdot a_{Cl^-}^3$$
$$= (m\gamma_{[Co(NH_3)_6]^{3+}})(3m\gamma_{Cl^-})^3$$
$$= 27m^4\gamma_{[Co(NH_3)_6]^{3+}} \cdot \gamma_{Cl^-}^3 \qquad (1)$$

When the mean activity coefficient of the salt is expressed by $\gamma_\pm$, the formula 1 is replaced by

$$K = 27m^4\gamma_\pm^4 \qquad (1')$$

In order to calculate K, it is necessary to know the mean activity coefficient of the hexamminecobalt(III) chloride in each molality. It was obtained by interpolation

* Read at the 11th Annual Meeting of the Chemical Society of Japan, held in April, 1958.

1) J. N. Brönsted and Agnes Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921).

2) M. Mori and R. Tsuchiya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1164 (1958).

3) W. C. Fernelius, "Inorganic Syntheses," Vol. II, (1946), p. 216

4) M. Mori and M. Shibata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1044 (1954).

TABLE I. SOLUBILITY OF HEXAMMINECOBALT(III) CHLORIDE

Temp.(°C)	Solubility C	Molality m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^5$	log K
10	0.2018	0.2073	3.534	0.1371	1.763	$\bar{5}$.2463
15	0.2336	0.2411	3.472	0.1276	2.417	$\bar{5}$.3833
20	0.2659	0.2758	3.413	0.1194	3.173	$\bar{5}$.5015
25	0.2915	0.3033	3.356	0.1143	3.898	$\bar{5}$.5908
30	0.3289	0.3446	3.300	0.1079	5.159	$\bar{5}$.7126
35	0.3557	0.3741	3.247	0.1045	6.308	$\bar{5}$.7999

TABLE II. SOLUBILITY OF HEXAMMINECOBALT(III) BROMIDE

Temp.(°C)	Solubility C	Molality m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^7$	log K
10	0.04487	0.04503	3.534	0.2749	6.338	$\bar{7}$.8020
15	0.05161	0.05199	3.472	0.2607	9.112	$\bar{7}$.9596
20	0.05916	0.05986	3.413	0.2447	12.43	$\bar{6}$.0944
25	0.06678	0.06788	3.356	0.2304	16.15	$\bar{6}$.2082
30	0.07450	0.07607	3.300	0.2189	20.75	$\bar{6}$.3172

TABLE III. SOLUBILITY OF HEXAMMINECOBALT(III) NITRATE

Temp.(°C)	Solubility C	Molarity m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^7$	log K
10	0.03153	0.03137	3.534	0.3252	2.924	$\bar{7}$.4660
15	0.04129	0.04146	3.472	0.2885	5.526	$\bar{7}$.7424
20	0.05096	0.05138	3.413	0.2620	8.865	$\bar{7}$.9477
25	0.06169	0.06248	3.356	0.2390	13.42	$\bar{6}$.1278
30	0.07103	0.07225	3.300	0.2230	18.29	$\bar{6}$.2622

TABLE IV. SOLUBILITY OF HEXAMMINECOBALT(III) PERCHLORATE

Temp.(°C)	Solubility C	Molality m	$1/T\times10^3$	$\gamma_\pm$	$K\times10^5$	log K
10	0.01344	0.01342	3.534	0.4494	3.570	$\bar{8}$.5526
15	0.01651	0.01652	3.472	0.4189	6.191	$\bar{8}$.7918
20	0.02032	0.02039	3.413	0.3865	10.41	$\bar{7}$.0175
25	0.02539	0.02556	3.356	0.3544	18.17	$\bar{7}$.2595
30	0.03207	0.03240	3.300	0.3205	31.39	$\bar{7}$.4968

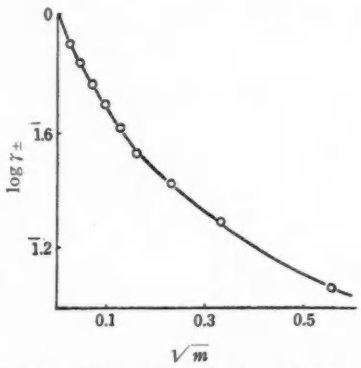

Fig. 1. The mean activity coefficient of hexamminecobalt(III) chloride.

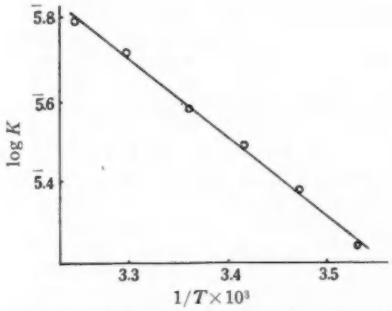

Fig. 2. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) chloride.

and extrapolation of the curve in Fig. 1 obtained in the preceding paper[2] which gave the relationship between the mean activity coefficient and the molality for hexamminecobalt(III) chloride. The logarithm of K calculated by the formula 1 and given in Table I is plotted against the reciprocal of the absolute temperature in Fig. 2, which shows an almost straight line. By the least square method the equation of this straight line is computed as follows:

$$\log K = 1.8823 - 1873/T \qquad (2)$$

From the inclination of this straight

line or the coefficient of $1/T$, the heat of solution is obtained as $\Delta H=8567$ cal.

As the heat of solution, the value of 9.0 kcal. was determined calorimetrically[5]; this value is in good agreement with our value.

By Kapustinskiĭ[6], the lattice energy of a complex salt was given by,

$$U_{ca}=287.2\frac{\Sigma n\cdot z_1\cdot z_2}{r_1+r_2}\left(1-\frac{0.345}{r_1+r_2}\right) \quad (3)$$

where n is the number of ions dissociated, z_1 and z_2 are the charges of cation and anion, and r_1 and r_2 are the radii of cation and anion, respectively. By Fajans[7], the heat of solution, L, was given by,

$$L = L_1 + L_2 - U_{ca} \quad (4)$$

in which L_1 and L_2 are the heat of hydration of cation and anion. By using these two formulae 3 and 4, the heat of solution of hexamminecobalt(III) chloride is calculated as $\Delta H=13.53$ kcal., which is a little larger than the value, 8567 cal., calculated from the solubility data.

From the heat of formation of solid hexamminecobalt (III) chloride, $\Delta H=-274.1$ kcal.[5], that of the hexamminecobalt(III) ion in unit activity, $\Delta H=-146$ kcal.[8], and that of chloride ion in unit activity, $\Delta H=-40.023$ kcal.[9], given in the literature, the heat of solution of this complex salt can also be calculated as $\Delta H=8031$ cal., which is again in agreement with the value 8567 cal. calculated above.

The standard free energy change of the solution, ΔG°, is computed by the following formula using the value of K given in formula 2,

$$\Delta G^\circ=-RT\ln K=8567-8.61T \quad (5)$$

Values of the standard free energy change of solution at 25°C (298°K), $\Delta G^\circ_{298}=6003$ cal. and the entropy change of solution at 25°C, $\Delta S^\circ_{298}=8.61$ e. u. are obtained; these formulae have never before been found in the literature.

As the standard free energy of formation of the hexamminecobalt(III) ion at 25°C the value of $\Delta G^\circ_{298}=-54.5$ kcal.[10] was already known. By using this value and the heat of formation of this ion, $\Delta H=-146$ kcal.[8], the standard free energy of formation of the ion as the function of temperature is calculated as,

$$\Delta G^\circ=-146000+307T \quad (6)$$

From the formulae 5 and 6 and the standard free energy of formation of chloride ion in unit activity, that of hexamminecobalt(III) chloride in the solid state is calculated as

$$\Delta G^\circ=-274660+402.9T$$

and the value of $\Delta G^\circ_{298}=-154.55$ kcal. is obtained.

Hexammincobalt(III) Bromide. — The change when the hexamminecobalt(III) bromide was dissolved into water is expressed by,

$$[Co(NH_3)_6]Br_3(s)=[Co(NH_3)_6]Br_3(aq.\,a)$$
$$=[Co(NH_3)_6]^{3+}(aq.)+3Br^-(aq.)$$

The equilibrium constant of the solution, K, is deduced in the same manner as in the formula 1, if m and $\gamma_\pm$ are replaced by those of the bromide.

If the activity coefficients of the above cation and anion are expressed by γ_+ and γ_-, the mean activity coefficient of the salt, $\gamma_\pm$, is given by $\gamma_\pm=\sqrt[4]{\gamma_+\cdot\gamma_-^3}$. As the activity coefficient of the bromide ion is the same as that of the chloride ion according to Kielland's table[11], the mean activity coefficient of the hexamminecobalt(III) bromide is assumed to be the same as that of the chloride. Then the value in each molality was obtained by the interpolation of the curve for hexamminecobalt(III) chloride shown in Fig. 1. By using this $\gamma_\pm$ and the molality determined

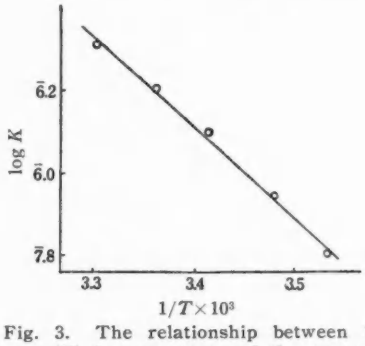

Fig. 3. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) bromide.

5) K. B. Yatsimirskiĭ and L. L. Pankowa, *Zhur. Obshchei Khim.*, **19**, 617 (1949); K. B. Yatsimirskiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 162.

6) A. F. Kapustinskiĭ, *Zhur. Obshchei Khim.*, **13**, 497 (1943); K. B. Yatsimirskiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 14.

7) K. B. Yatsimirskiĭ, ibid., (1956), p. 44.

8) K. B. Yatsimirskiĭ, ibid., (1956), p. 161.

9) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington, D. C. (1952), p. 21.

10) A. B. Lamb and A. T. Larson, *J. Am. Chem. Soc.*, **42**, 2038 (1920).

11) J. Kielland, ibid., **59**, 1675 (1937).

from the solubility measurement, the equilibrium constant K given in Table II was calculated.

The plots of $\log K$ against the reciprocal of the absolute temperature are shown as a straight line in Fig. 3, and the equation of the straight line is calculated by the least square method as

$$\log K = 2.1911 - 2378/T \qquad (7)$$

From this equation the heat of solution is obtained as $\Delta H = 10.026$ kcal.

The heat of solution determined calorimetrically is 12.7 kcal.[5] and that calculated by Kapustinskii's formula 3 and Fajans' one 4, is 13.90 kcal., both of which are a little higher than our value, 10.026 kcal. From the heat of formation of hexamminecobalt(III) bromide in the solid state, $\Delta H = -244.5$ kcal.[5], that of the hexamminecobalt(III) ion in unit activity[8] already given and that of the bromide ion in unit activity, $\Delta H = -28.90$ kcal.[12], the heat of solution of the complex bromide is calculated as 11.8 kcal., which is closer to our value 10.026 kcal. than the two former ones, 12.7 and 13.90 kcal.

The standard free energy change of solution is calculated by the formula 7 as

$$\Delta G^\circ = 10026 - 7.56T \qquad (8)$$

and the value of $\Delta G^\circ_{298} = 7772$ cal. and $\Delta S^\circ_{298} = 7.56$ e. u. are obtained.

From the formulae 8 and 6 and the standard free energy of formation of the bromide ion in unit activity, that of hexamminecobalt(III) bromide in the solid state is calculated as

$$\Delta G^\circ = -242726 + 358.09T$$

and the value of $\Delta G^\circ_{298} = -136.12$ kcal. is obtained.

Hexamminecobalt(III) Nitrate.—As the activity coefficient of the nitrate ion is the same as that of the chloride ion according to Kielland's table[11], the mean activity coefficient of the hexamminecobalt(III) nitrate in each molality is obtained in the same way as that for the bromide from Fig. 1, and the equilibrium constant, K, listed in Table III was calculated by the formula 1′.

The plots of $\log K$ against the reciprocal of the absolute temperature are shown in Fig. 4 as a straight line and the equation of the straight line is calculated as

$$\log K = 3.3797 - 2774/T \qquad (9)$$

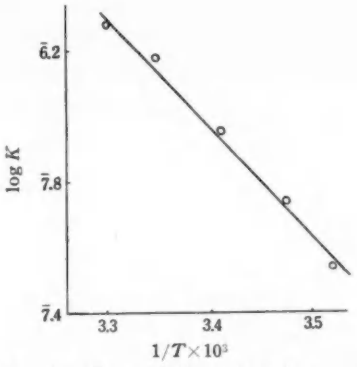

Fig. 4. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) nitrate.

From this equation, the heat of solution is obtained as $\Delta H = 15.558$ kcal. The value found in the literature[5] is 17.9 kcal. and that which was calculated from the heat of formation of hexamminecobalt(III) nitrate in the solid state, $\Delta H = -311.5$ kcal.[5], that of the hexamminecobalt(III) ion in unit activity[8] already given and that of the nitrate ion in unit activity, $\Delta H = -49.372$ kcal.[13], is 17.384 kcal., both of which are a little higher than our value, 15.558 kcal.

The standard free energy change of solution is calculated by the formula 9 as

$$\Delta G^\circ = 15558 - 25.63T \qquad (10)$$

and the value of $\Delta G^\circ_{298} = 7918$ cal. and $\Delta S^\circ_{298} = 25.63$ e. u. are obtained.

From the formulae 10 and 6 and the standard free energy of formation of the nitrate ion in unit activity, that of hexamminecobalt(III) nitrate in the solid state is calculated as

$$\Delta G^\circ = -309674 + 563.72T$$

and the value of $\Delta G^\circ_{298} = 141.68$ kcal. is obtained.

Hexamminecobalt(III) Perchlorate.—According to Kielland's table[11] the activity coefficient of perchlorate ion is different no more than 0.4% even in the molality of 0.01 from that of the chloride ion. Therefore, the activity coefficient of the hexamminecobalt(III) chloride shown in Fig. 1 was used in the place of that of the perchlorate to calculate the equilibrium constant, K. The values of $\log K$ are plotted against $1/T$ in Fig. 5, and the straight line obtained can be represented by the following equation:

12) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington, D. C. (1952), p. 27.

13) F. D. Riossini et al., ibid., (1952), p. 53.

TABLE V. THERMODYNAMIC FUNCTIONS FOR HEXAMMINECOBALT (III) COMPLEXES

Complex salts	Heat of solution	Free energy change of solution	Standard free energy of formation
$[Co(NH_3)_6]Cl_3$	8.567 kcal.	6.003 kcal.	−154.55 kcal.
$[Co(NH_3)_6]Br_3$	10.026	7.772	−136.12
$[Co(NH_3)_6](NO_3)_3$	15.558	7.918	−141.68
$[Co(NH_3)_6](ClO_4)_3$	18.533	9.080	− 71.40

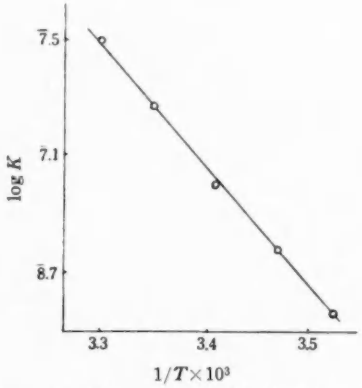

Fig. 5. The relationship between the equilibrium constant and the temperature for hexamminecobalt(III) perchlorate.

$$\log K = 4.0396 - 3226/T \qquad (11)$$

The heat of solution is obtained as $\Delta H = 18.53$ kcal. The value found in the literature, 22.5 kcal.[14], and that calculated by the equations 3 and 4, 21.54 kcal., are both higher than our value, 18.53 kcal.

The standard free energy change of solution is calculated from 11 as

$$\Delta G^\circ = 18533 - 31.71T \qquad (12)$$

and the value of $\Delta G^\circ_{298} = 9080$ cal., and $\Delta S^\circ_{298} = 31.71$ e. u. are obtained.

From the formulae 12 and 6 and the standard free energy of formation of the perchlorate ion, that of hexamminecobalt-(III) perchlorate in the solid state is calculated as

$$\Delta G^\circ = -258763 + 628.96T$$

and the value of $\Delta G^\circ_{298} = -71.46$ kcal. is obtained.

14) A. F. Kapustinskiĭ and K. B. Yatsimirskiĭ, *Zhur. Fiz. Khim.*, **22**, 1271 (1948); K. B. Yatsimirsikiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 1632.

The thermodynamic values obtained for the above four hexamminecobalt(III) salts are summarized in Table V.

As shown in this table, both the heat of solution and the free energy change of the solution become greater in the order of hexamminecobalt(III) chloride, bromide, nitrate and perchlorate. This means that the affinity of these complexes toward water becomes greater in this order. However, the standard free energy of their formation increases in the order of chloride, nitrate, bromide and perchlorate and this means that the thermodynamic stability becomes lower in this order; that is, chloride is the most stable among the above four salts in the solid state.

Summary

The solubilities of hexamminecobalt(III) chloride, bromide, nitrate and perchlorate were measured at 10~35°C. From the solubility measurements the relationships between the equilibrium constant of the solution and the temperature were calculated. The heats of solution calculated from these data agreed approximately with the values given in the literature and those calculated by using formulae of Kapustinskiĭ and Fajans.

The free energy changes of formation of these complexes in the solid state were calculated for the first time. It is concluded from the results that the stability of these salts decreases in the following order:

$[Co(NH_3)_6]Cl_3 > [Co(NH_3)_6](NO_3)_3 > [Co(NH_3)_6]Br_3 > [Co(NH_3)_6](ClO_4)_3$

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*Thermodynamic Studies on Cobalt Complexes. III. Thermal Dissociation of Hexamminecobalt(III) Chloride and Chloropentamminecobalt(III) Chloride**

By Motoshichi MORI and Ryokichi TSUCHIYA

(Received September 17, 1958)

Compared with a great number of studies on the reaction of complex salts in the aqueous solution, the investigations on the thermal decomposition of complexes in the solid state are few. These include studies on ammines of cobalt[1,2], nickel[3], platinum[4] and indium[5] and on nitroammines of platinum[6] and cobalt[7,8]. Among these studies the data on dissociation pressure were reported only for cobalt- and nickelammine complexes[1,3] and thermodynamic discussion of them has never been made. For this reason we started the present study and determined the dissociation pressure of hexamminecobalt-(III) chloride and chloropentamminecobalt-(III) chloride. The free energy change of dissociation of the former complex was calculated and the standard free energy of formation of the latter complex was obtained.

Experimental

Hexamminecobalt(III) chloride was prepared by Bjerrum's method[9] and chloropentamminecobalt-(III) chloride, by the method of Jörgensen[10]. The apparatus used for the determination of the dissociation pressure is shown in Fig. 1.

After the sample was put into the reaction vessel, made of heat resistant borosilicate glass, A, the whole apparatus was evacuated. The cocks B and C were closed and the temperature of the electric furnace F was held at the desired constant temperature by an automatic regulator. The dissociation pressure was determined by the manometer M.

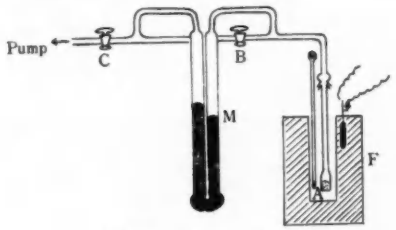

Fig. 1. Apparatus.

Results and Discussion

Dissociation Pressure of Hexamminecobalt(III) Chloride. — The dissociation pressure of hexamminecobalt(III) chloride was measured at several temperatures in the range of 83~173°C. As we found that the decomposition products consist of chloropentamminecobalt(III) chloride and ammonia, but not of cobaltous chloride, the decomposition reaction can be expressed by the following equation,

$$[Co(NH_3)_6]Cl_3(s) = [Co(NH_3)_5Cl]Cl_2(s) + NH_3(g)$$

The values of dissociation pressure determined for hexamminecobalt(III) chloride are listed in Table I.

Biltz[1] reported that the decomposition of hexamminecobalt(III) chloride began at 175~180°C and chloropentamminecobalt-(III) chloride was formed at 216~220°C. Clark et al[2]. reported that the decomposition began at 173°C and ammonium chloride appeared at 181°C. However, we detected the evolution of ammonia at 160°C by passing the decomposition gas into water containing phenolphthalein, and could determine the dissociation pressure at a temperature lower than that pointed out by Biltz[1] and Clark[2].

* Read at the Symposium on Co-ordination Compounds sponsored by the Chemical Society of Japan, held in Nov., 1957.

1) W. Biltz, *Z. anorg. Chem.*, **83**, 177 (1913).
2) G. L. Clark, A. J. Quick and W. D. Harkins, *J. Am. Chem. Soc.*, **42**, 2483 (1920).
3) W. Biltz and B. Fetkenheuer, *Z. anorg. Chem.*, **83**, 163 (1913).
4) A. A. Grinberg and B. V. Ptitzuin, *Izv. Inst. Platin*, **9**, 73 (1932); *Chem. Abstr.*, **27**, 1290 (1933).
5) V. G. Tronev and A. P. Kochetkova, *Khim. Redkikh Elementov, Akad. Nauk S. S. S. R., Inst. Obshchei i Neorg. Khim.*, (1957), No. 3, p. 87; *Chem. Abstr.*, **52**, 2634b (1958).
6) L. A. Chugaev and S. S. Kil'tuinovich, *Izv. Inst. Platin*, **2**, 70 (1921); *Chem. Abstr.*, **20**, 2961 (1926).
7) A. V. Ablov and N. I. Lobanov, *Zhur. Obshchei Khim.*, **25**, 648 (1955); *Chem. Abstr.*, **49**, 12170h (1955).
8) A. V. Ablov, E. A. Popa and T. A. Malkova, *Zhur. Neorg. Khim.*, **1**,2716 (1956); *Chem. Abstr.*, **50**, 13634i (1956).
9) W. C. Fernelius, "Inorganic Syntheses", Vol II. McGraw Hill Book Co., Inc., New York, N. Y. (1946), p. 216.
10) S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 281 (1892).

TABLE I. DISSOCIATION PRESSURE OF HEXAMMINECOBALT(III) CHLORIDE

Temp.(°C)	$1/T\times10^3$	Dissociation pressure (mmHg)	$\log p_{mm}$
83	2.808	0.70	−0.1549
92	2.739	1.15	0.0607
102	2.666	1.45	0.1614
114	2.583	2.19	0.3404
124	2.518	2.89	0.4609
129	2.487	3.49	0.5428
133	2.462	3.94	0.5955
138	2.432	4.59	0.6618
143	2.403	5.33	0.7267
149	2.369	6.04	0.7810
153	2.347	6.98	0.8439
158	2.320	7.73	0.8882
162	2.298	8.87	0.9479
168	2.267	10.33	1.0141
173	2.242	12.21	1.0867
176	2.227	14.26	1.1541

Biltz[1] observed 14 mmHg as the dissociation pressure of hexamminecobalt(III) chloride at 174°C, which is relatively close to our value, but he did not measure it at a temperature lower than 174°C. On the other hand, it was found by us that ammonium chloride began to form at about 170°C and the decomposition pressure rapidly increased at higher temperatures.

The logarithm of the dissociation pressure was plotted against the reciprocal of the absolute temperature (Curve a in Fig. 2). The obtained curve is approximately linear except the two points at 173 and 176°C. The equation of the straight line is calculated by the least square method as follows:

$$\log p_{mm} = 5.7705 - 2101.40/T \qquad (1)$$

From this equation the heat of dissociation is obtained as $\Delta H = 9612$ cal.

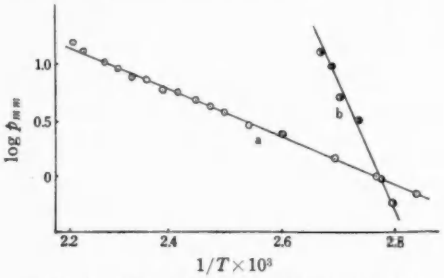

Fig. 2. The relationship between the dissociation pressure and the temperature for
a: hexamminecobalt(III) chloride
b: chloropentamminecobalt(III) chloride.

Biltz[1] obtained the value of about 18 kcal. as the heat of dissociation from his data determined at 174~216°C by means of the Nernst formula, but we recalculated the value of 28 kcal. from his data.

If the value of $\Delta H = 9612$ cal. determined above at the temperature in the range of 83~173°C is assumed to be approximately equal to that at 25°C, it agrees fairly well with the value of 8.56 kcal. calculated from the heats of formation of $[Co(NH_3)_6]Cl_3(s)$, (−274.1 kcal.[11]), $[Co(NH_3)_5Cl]Cl_2(s)$, (−254.5 kcal.[12]) and $NH_3(g)$ (−11.04 kcal.[13]).

The standard free energy change of decomposition calculated by the formula 1 is:

$$\Delta G^\circ = -RT\ln p = 9612 - 13.218T \qquad (2)$$

The values of $\Delta G^\circ_{298} = 5672$ cal. and $\Delta S^\circ_{298} = 13.22$ e. u. are obtained.

The standard free energy of formation of complex salts in the solid state has never been known except that of $[Co(NH_3)_6]Cl_3(s)$, which was calculated by the present authors from the solubility data in the preceding paper[14]. By using this value and the equation 2 the standard free energy of formation of $[Co(NH_3)_5Cl]Cl_2(s)$ in the solid state is calculated to be:

$$\Delta G^\circ = -254008 + 365.99T$$

and the value of $\Delta G^\circ_{298} = -144.90$ kcal. is obtained.

Dissociation Pressure of Chloropentamminecobalt(III) Chloride. — The dissociation pressure of chloropentamminecobalt-(III) chloride was measured by the same apparatus as that shown in Fig. 1. The results are given in Table II.

TABLE II. DISSOCIATION PRESSURE OF CHLOROPENTAMMINECOBALT(III) CHLORIDE

Temp.(°C)	$1/T\times10^3$	Dissociation pressure (mmHg)	$\log p_{mm}$
88	2.769	0.50	−0.3010
93	2.732	1.49	0.1732
96	2.709	3.08	0.4886
99	2.687	5.93	0.7731
101	2.673	9.51	0.9782
103	2.659	12.15	1.0846

11) K. B. Yatsimirskiĭ and L. L. Pankowa, *Zhur. Obshchei Khim.*, **19**, 617 (1949); K. B. Yatsimirskiĭ, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 162.
12) A. B. Lamb and J. P. Simmons, *J. Am. Chem. Soc.*, **43**, 2188 (1921).
13) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances", Reinhold Publishing Corp., New York, N. Y. (1936).
14) M. Mori, R. Tsuchiya and Y. Okano, This Bulletin, **32**, 462 (1959).

Biltz[1] found that chloropentamminecobalt(III) chloride decomposed at 180~220°C, but our results show that the decomposition takes place at a lower temperature. In contrast to hexamminecobalt(III) chloride, the increase of the dissociation pressure of chloropentamminecobalt(III) chloride with the rise of temperature is quite large. In other words, although the dissociation pressure of chloropentamminecobalt(III) chloride is less than that of hexamminecobalt(III) chloride at a temperature lower than 90°C, the thermal dissociation of the former exceeds that of the latter at a temperature higher than 92°C, and the dissociation pressure of the former at 103°C is nearly the same as that of the latter at 173°C. It is concluded from these facts that chloropentamminecobalt(III) chloride is stable at a temperature below 90°C and becomes suddenly unstable at a temperature above 192°C.

The plots of the logarithm of the dissociation pressure against the reciprocal of the absolute temperature give a straight line as shown by the line b in Fig. 2. The equation of the straight line is calculated as follows:

$$\log p_{mm} = 36.4869 - 13288.3/T$$

From this equation as the heat of dissociation the value of $\Delta H = 60.78$ kcal. is obtained. It is in good agreement with the value, 60.84 kcal., which is calculated from the heats of formation of components of the following dissociation reaction,

$$[Co(NH_3)_5Cl]Cl_2(s) = CoCl_2(s) + 1/6\,N_2(g) + NH_4Cl(s) + 11/3\,NH_3(g)$$

$\Delta H_{f[Co(NH_3)_5Cl]Cl_2} = -254.5$ kcal.[12]

$\Delta H_{fCoCl_2} = -77.8$ kcal.[15]

$\Delta H_{fNH_4Cl} = -75.38$ kcal.[13] and

$\Delta H_{fNH_3} = -11.04$ kcal.[13]

The Rate of Thermal Dissociation of Hexamminecobalt(III) Chloride.—The rate of the thermal dissociation of this complex was determined by tracing the pressure change of ammonia produced in the decomposition by the apparatus shown in Fig. 1. The results are shown in Table III and Fig. 3.

The velocity constant k at the time when the dissociation begins to take place is given by the tangent of the velocity curve at zero point in Fig. 3. The plots of logarithm of the velocity constant against the reciprocal of the absolute temperature give a straight line as shown in Fig. 4, from which the value of 17.98

TABLE III. RATE OF DISSOCIATION OF HEXAMMINECOBALT(III) CHLORIDE

Temp.(°C)	153	163	173
Time(min.)	Dissociation pressure p mmHg		
3	—	1.05	1.50
5	0.95	1.55	2.35
10	1.65	2.59	3.64
15	2.29	3.14	4.54
20	2.84	3.58	5.18
25	—	3.98	5.53
30	3.14	4.33	5.83
40	3.54	4.98	6.67
50	3.74	5.33	7.32
1(hr.)	3.99	5.58	7.67
1.5	4.44	6.17	9.01
2	4.84	6.47	10.26
2.5	5.13	7.02	10.86
3	5.28	7.42	11.31
4	5.83	—	11.55
k	0.2005	0.3390	0.5220
$\log k$	$\bar{1}.3021$	$\bar{1}.5302$	$\bar{1}.7177$
$1/T\times10^3$	2.347	2.293	2.242

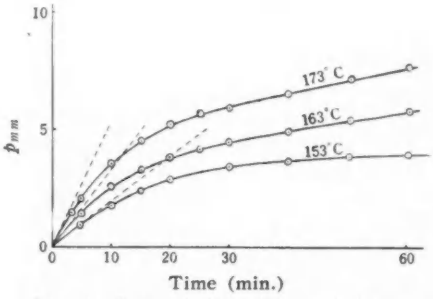

Fig. 3. Rate of dissociation of hexamminecobalt(III) chloride.

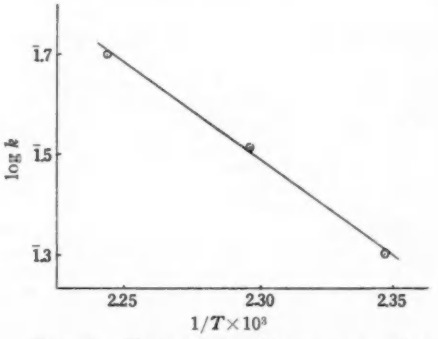

Fig. 4. The relationship between the velocity constant and the temperature for hexamminecobalt(III) chloride.

15) K. Sano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **58**, 370 (1937).

kcal. is obtained as the activation energy of the thermal dissociation of hexamminecobalt(III) chloride.

The Rate of Thermal Dissociation of Chloropentamminecobalt(III) Chloride.— The determination was made by the same method as that used in the above experiment for hexamminecobalt(III) chloride. The results are shown in Table IV and Fig. 5.

The plots of the logarithm of the velocity constant k at the time when the dissociation begins to take place against the reciprocal of the absolute temperature give a straight line as shown in Fig. 6, from which the value of 54.06 kcal. is obtained as the activation energy of the thermal dissociation of chloropentamminecobalt(III) chloride.

TABLE IV. RATE OF DISSOCIATION OF CHLOROPENTAMMINECOBALT(III) CHLORIDE

Temp.(°C)	96	100	103
Time(min.)	Dissociation pressure p mmHg		
2	—	—	0.25
5	—	0.35	0.60
8	—	—	0.90
10	0.40	0.65	1.10
15	—	0.90	1.55
20	0.65	1.10	2.05
25	—	1.30	2.29
30	0.95	1.50	2.49
40	1.10	1.75	3.34
50	1.35	2.00	3.83
1(hr.)	1.44	2.19	4.23
1.5	1.78	2.69	5.78
2	1.93	3.14	6.57
2.5	2.19	3.64	7.42
3	2.45	3.99	8.27
4	2.58	4.29	9.31
k	0.0354	0.0782	0.135
$\log k$	$\bar{2}.5490$	$\bar{2}.8932$	$\bar{1}.1303$
$1/T\times10^3$	2.709	2.680	2.659

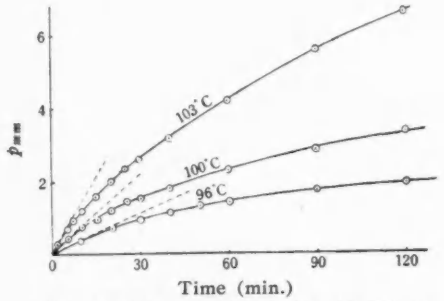

Fig. 5. Rate of dissociation of chloropentamminecobalt(III) chloride.

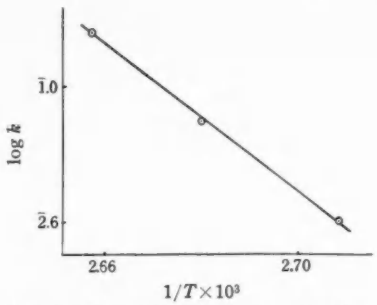

Fig. 6. The relationship between the velocity constant and the temperature for chloropentamminecobalt(III) chloride.

As shown above, the heat of dissociation and the activation energy of chloropentamminecobalt(III) chloride are very high compared with those of hexamminecobalt(III) chloride. These data give an explanation for the fact that chloropentamminecobalt(III) chloride produced in the thermal dissociation of hexamminecobalt(III) chloride does not suffer from further decomposition so far as the latter is present, even if the dissociation pressure of the former is very high.

Summary

1. The thermal dissociation of hexamminecobalt(III) and chloropentamminecobalt(III) chlorides was studied. The heats of dissociation calculated from the the data of dissociation pressure determined are in good agreement with the values calculated from other sources.

2. The free energy change of dissociation of hexamminecobalt(III) chloride was calculated and by combining this value with the standard free energy of formation of that complex previously obtained, the standard free energy of formation of chloropentamminecobalt(III) chloride in the solid state was determined.

3. The rate of the thermal dissociation of hexamminecobalt(III) and chloropentamminecobalt(III) chlorides was determined and the activation energies of the dissociation were calculated.

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Normal Stress Effects in Polymer Solutions. I. Measurements in a Parallel Plate Instrument

By Mikio TAMURA, Michio KURATA and Tadao KOTAKA

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It is well noted that a visco-elastic fluid under steady shear flow usually generates not only shearing stress but also normal stresses. Thus, the essential requirement for obtaining the complete information for flow behavior of such a fluid is the development of the *goniometry of flow*, or in other words, the development of experimental procedures for the determination of all stress components, i.e., shearing stress and normal stresses[1,2].

In this report, as the first step of the stress-goniometry of flow, we will describe some findings on the normal stress measurements in a parallel plate instrument. Correlations between observed normal pressure and dimension of the instrument, and influences of secondary effects which inevitably arise in the course of measurements will be discussed at some length[3]. Detailed descriptions of the data and their physical interpretations will be published in a subsequent paper[4].

Padden and DeWitt[5], and recently Markovitz and Williamson[6] have suggested that the concentration and temperature dependencies of normal stress should be expressible in terms of "*reduced variables*". These suggestions are tested with the data obtained in our measurements.

Experimental

Instrument and Principles.—A parallel plate instrument used in this study is shown in Fig. 1. The figure itself is self-explanatory. An outer cup containing a test fluid is rotated at a steady speed within the range of 5 to 170 rpm by driving through a pulley and belt system by a 1/2 H. P. induction motor. The rotating bob is held at a distance of one centimeter or less above the cup. The dimensions of two outer cups and three inner bobs used in this study are listed in Table I. When the cup is rotated, the fluid, if it shows the normal stress effect, rises in the manometer tubes mounted on the stationary bob and reaches equilibrium levels. Equilibrium heights of the fluid were read by a travelling microscope. The non-parallelism and the non-concentricity of two plates, especially the former, largely affect the pressure distribution and disturb the quantitative measurements. A con-

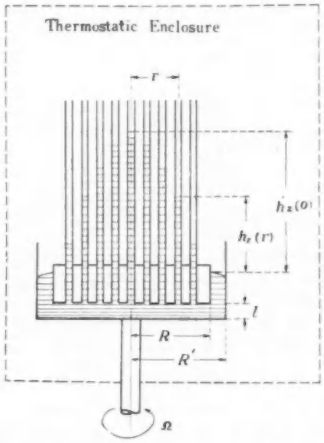

Fig. 1. Schematic diagram of the parallel plate instrument.

TABLE I. DIMENSIONS OF BOBS AND CUPS FOR NORMAL STRESS MEASUREMENTS

	Radius cm.	Manometer tubes		
		Number	Diameter cm.	Spacing cm.
Bob A	5.0	9	0.5	1.0
Bob B	6.5	13	0.2	0.8
Bob C	7.0	15	0.2	0.8
Cup 1	6.0			
Cup 2	8.0			

1) The general review on this subject is obtained in the following article: M. Kurata, "The Weissenberg Effect", in Kobunshi-Jikkengaku-Koza, Vol. V, ed. S. Kambara, Kyoritsu Publishing Co., Tokyo (1958), Chap. 15.

2) See also, A. Jobling and J. E. Roberts, "The Goniometry of Flow and Rupture", in Rheology Vol. II, ed. F. Eirich, Academic Press, New York (1958), Chap. 14.

3) Works of similar nature were developed by Greensmith and Rivlin, but they are different from ours in the standpoint and the approach to the problem. H. W. Greensmith and R. S. Rivlin, *Phil. Trans. Roy. Soc. (London)*, **245**, 399 (1953).

4) T. Kotaka, M. Kurata and M. Tamura, in preparation.

5) F. J. Padden and T. W. DeWitt, *J. Appl. Phys.*, **25**, 1086 (1954).

6) H. Markovitz and R. B. Williamson, *Trans. Soc. Rheology*, **1**, 25 (1957).

dition free from such disturbances is easily attained by making sure that the symmetry in pressure distribution is established and that the pressure values are kept unchanged by clockwise and counterclockwise rotations at the same speed. The temperature at which the measurements were run was roughly controlled within ± 1.0°C by a simple thermostatic enclosure.

The normal pressure is correlated to the normal stresses by the relation of force equilibrium in torsional shear flow as follows:

$$-\frac{\partial P_z(r)}{\partial \ln r} = \sigma_{11} - \sigma_{33} + \frac{\partial(\sigma_{22}-\sigma_{33})}{\partial \ln r} \tag{1}$$

or in the integral form

$$\Delta P_z(r) = P_z(0) - P_z(r) = \int_0^r (\sigma_{11}-\sigma_{33})\frac{dr}{r} + \sigma_{22} - \sigma_{33} \tag{2}$$

and

$$P_z(0) - P' = \int_0^R (\sigma_{11}-\sigma_{33})\frac{dr}{r} \tag{3}$$

where $P_z(r)$ denotes the pressure exerted on the stationary bob of radius R at the distance r from the rotating axis, P' denotes the pressure exerted on the fluid in the gap from the outside, σ_{ii} ($i=1,2,3$) denotes the normal stress component parallel to the direction of flow ($i=1$), and perpendicular to the shearing surface ($i=2$), and perpendicular to both ($i=3$), respectively. It should be noted here that in the derivation of the above equations the influences of the centrifugal force, and of disturbances of flow arising from edge effects were all neglected. It is readily seen that, if the state of flow were ideally torsional shear and undesirable disturbances were depressed within the experimental error, the left hand sides of the equations from 1 to 3 should be dependent on the rate of shear, $D=r\Omega/l$, alone. Here r is the distance from the axis, Ω is the angular velocity of rotation and l is the gap between two plates.

Materials.—Solutions of a commercial sodium carboxymethylcellulose (Na-CMC; Harcules, Cellulose Gum Type 70 sp-High) obtained through the courtesy of Dr. H. Inagaki of this University were mainly used in this study. Its molecular weight was about 10^5, and the range of degree of carboxymethylation was from 0.65 to 0.95. The data obtained on the solutions of commercial methylcellulose* (Interchemical, Methocell 4000 cp: $\bar{M}_v \sim 10^5$, $D.S.\sim 0.92$) in water and polystyrene* (Lustrex Hi-Flow 77, $\bar{M}_v \sim 10^5$) in decalin are also described for the sake of comparison.

Results and Discussion

Some Geometrical Studies in a Parallel Plate Instrument.—$h_z(0)$ *vs.* Ω *Relations*: *the Centrifugal Force Effect*:—With the combination of bob A and cup 1, we first read $h_z(0)$ against the rotational velocity, Ω, with various gaps, l, on solution of 2g. Na-CMC in 100ml. water (1.97 wt.%). The results are shown by solid lines in Fig. 2. If the curves of $h_z(0)$ vs. Ω with different l are replotted against the rate of torsion, Ω/l, they fall on a single reduced curve as shown by a broken line in Fig. 2. Close inspection, however, reveals that $h_z(0)$ value begins to deviate below the reduced curve when the rotational speed exceeds about 70~80 rpm irrespective of the gap, l. This tendency should be attributed mainly to the influence of the centrifugal force which repels the fluid outward in a radial direction and also acts as a rotational couple in r-z plane. The exact mathematical treatment of this effect is quite difficult, but in any case, the action of the centrifugal force may lower the $h_z(0)$ values, especially may lower them remarkably at a high velocity. Thus we may conclude that, to eliminate the effect of the centrifugal force, it is preferable to keep the rotational speed below about 70~80 rpm with a cup of this dimension ($R'=6.0$ cm.).

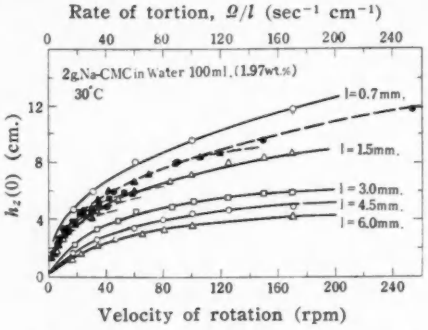

Fig. 2. $h_z(0)$ vs. velocity of rotation (solid lines) and $h_z(0)$ vs. rate of torsion, Ω/l (broken lines); Na-carboxymethylcellulose in water 1.97% at 20°C.

Pressure Distribution on a Stationary Bob: the Edge Effect:—In the derivation of Eqs. from 1 to 3, the influence arising from the side gap was simply replaced by an isotropic term P'. To check the validity of this assumption, measurements were performed with two different combinations of bob A ($R=5.0$ cm.) with cup 1 ($R'=6.0$ cm.), and bob A with cup 2 ($R'=8.0$ cm.) on solutions of Na-CMC-water, and the pressure distributions on the bob were compared. Fig. 3 indicates the pressure distributions, $h_z(r)$, with various velocities.

* Samples of methylcellulose and polystyrene were obtained through the courtesy of Toyo Ink Mfg. Co., Ltd., and Nagase and Co., respectively.

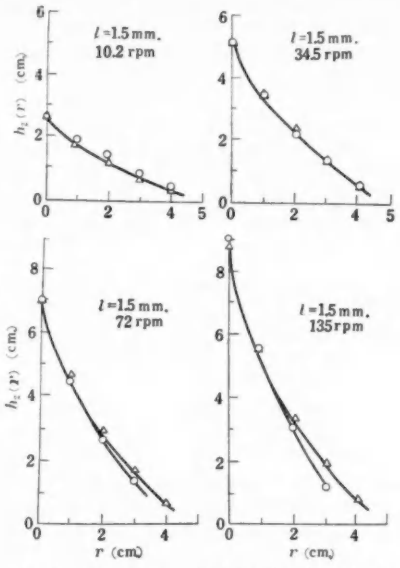

Fig. 3. Pressure distributions on a stationary plate (R=5.0 cm.) with cup 1 (R'=6.0 cm.)···Δ, and cup 2 (R'=8.0 cm.)···0. 1.97wt.%-CMC-water.

It is seen that when the rotational velocity is not so high the pressure distribution, $h_z(r)$, is practically unaffected by the difference in the side gap, but, the higher the velocity becomes (above 70 rpm), the more significant the deviation becomes. The pressure falls more rapidly in the larger cup. The plots of $h_z(0)$ vs. Ω/l, though the data are not shown here, are reduced on a single curve except at high speed and show no indication of edge effect.

Effect Arising from the Finite Size of Accesses of Manometer Tubes.—It might be expected that the presence of holes of manometer tubes on the base of a bob would disturb the flow pattern in their neighbor. Also for the finite size of accesses of manometers, the observed pressure does not represent a value at its center but the average over the area. That the quantitative estimation of this average with a parallel plate instrument is impracticable without the dependence of $h_z(r)$ on r (namely on the rate of shear) has been known. It can be said, however, that when the diameter of holes is larger, their influence is also greater. Actually, in our measurements, for the bob A (diameter of holes is 5 mm.) a slight but appreciable deviation was observed, while for the bob with smaller holes (diameter 2 mm.) no appreciable disturbance was observed. This had also been observed by Greensmith and Rivlin[3]. It is desirable to keep the size of holes as small as possible, but if too small, it becomes time-consuming for the fluid to attain equilibrium positions in each manometer.

The Normal Pressure Gradient $-\partial P_z(r)/\partial \ln r$ *vs. Rate of Shear* D.—Eqs. 1 and 2 indicate that the normal pressure difference, $\Delta P_z(r)$, or the normal pressure

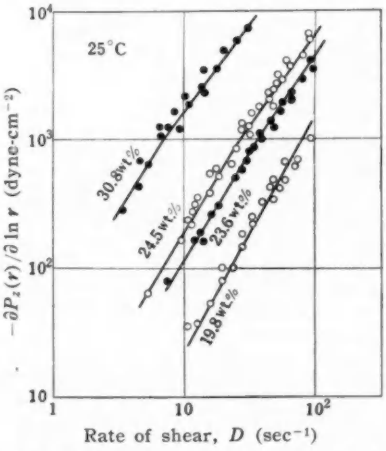

Fig. 4 (a). Normal pressure gradient, $-\partial P_z(r)/\partial \ln r$, as a function of rate of shear, D. Solutions of polystyrene in decalin.

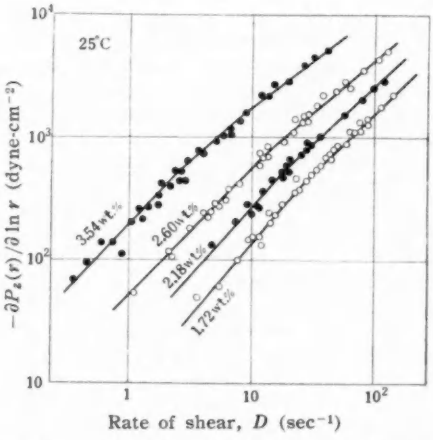

Fig. 4 (b). Normal pressure gradient, $-\partial P_z(r)/\partial \ln r$, as a function of rate of shear, D. Solutions of methylcellulose in water.

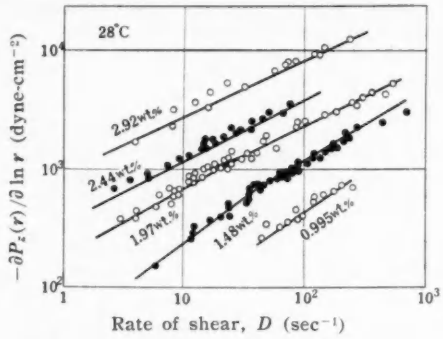

Fig. 4 (c). Normal pressure gradient, $-\partial P_z(r)/\partial \ln r$, as a function of rate of shear, D. Solutions of Na-carboxymethylcellulose in water.

gradient, $-(\partial P_z(r)/\partial \ln r)$**, should be a function of the rate of shear, $D=r\Omega/l$. Fig. 4 indicates the curves of $-\partial P_z(r)/\partial \ln r$ vs. D for three different polymer species, all of which show that the expected relations safely hold. Of course, the data which were beyond the limitations mentioned in the previous subsections were eliminated in the plots.

It should be noticed that the dependences of normal stresses on the rate of shear differ remarkably in each polymer species, which reflect the essential difference in characteristic rheological properties of those polymers. The detailed discussions will be given in our subsequent paper[4].

The Applicability of the Superposition Principle.—It has been suggested that from the normal stress data obtained on solutions of various concentrations and temperatures, a single reduced curve should be obtained by applying the superposition procedure which is currently used for the dynamic data[5,6]. In this case, reduced quantities are defined such as

$$[-\partial P_z(r)/\partial \ln r]_r = [-\partial P_z(r)/\partial \ln r] \cdot [T_0/Tf(c)]$$

and $$D_r = D\eta\, T_0/Tf(c)$$

where T is the absolute temperature, T_0 is a reference temperature, and η is the *zero shear* viscosity of the solution. $f(c)$ is a function of concentration, and was chosen by Padden and DeWitt[5] as $f(c)=c$ and by Markovitz and Williamson[6] as $f(c)=c/c_0$ for $c<c_0$ and $f(c)=c^2/c_0^2$ for $c\geq c_0$. The reduced plot of the data with solutions of methylcellulose in water is shown in Fig. 5, in which $T_0=298$°K and $f(c)=c$. It is seen that the reduction is not so satisfactory, but rather a systematic deviation is observed. Although results are not shown here, another choice of $f(c)$ improves the situation slightly. For another two polymer species, polystyrene in decalin and Na-CMC in water, the reductions are a little better than for methylcellulose in water, but again not so satisfactory.

On the basis of the cross-elasticity theory[4], the normal stresses and the apparent viscosity (=shearing stress/rate of shear) are given as follows:

$$-\frac{\partial P_z(r)}{\partial \ln r} = \sigma_{11}-\sigma_{33} = G\tau^2 D^2 \tag{4}$$

$$\eta = \sigma_{12}/D = G\tau \tag{5}$$

where G and τ are the shear modulus and the relaxation time of the solution, respectively. The superposition procedures are based on the following assumptions: the shear modulus and the relaxation time of the solution are dependent on such concentration and temperature that $G=G_0[Tf(c)/T_0f(c_0)]$ and $\tau=a_Ta_c\tau_0$. Here G_0 and τ_0 are the values of G and τ, respectively, at the reference temperature T_0 and concentration c_0. Introducing these assumptions into Eqs. 4 and 5, we obtain

$$-\frac{\partial P_z(r)}{\partial \ln r} = \frac{Tf(c)}{T_0f(c_0)} G_0\tau_0^2(a_Ta_cD)^2 \tag{6}$$

$$D\eta = \frac{Tf(c)}{T_0f(c_0)} G_0\tau_0(a_Ta_cD) \tag{7}$$

and

$$a_Ta_c = \frac{T_0f(c_0)}{Tf(c)}\frac{\eta}{\eta_0} \tag{8}$$

With the choice of such a reference state that η_0 and $f(c_0)$ are unity and a *zero shear* value for η, the reduced variables indicated before are determined.

It should be mentioned, however, that the above-mentioned definitions of reduced variables implicitly include such a further assumption namely that the reducing factors, $f(c)/f(c_0)$ and a_Ta_c, are independent of the rate of shear. This assumption may be valid in the case of a dynamic measurement if the amplitudes of vibrational motion are sufficiently small. On the other hand, in the steady flow measurements over wide range of rates of shear, this assumption may be improper, or valid only within a limited range of rates of shear, or of concentrations. Actually, the flow curves of polymer solutions

** Many experimental evidences show that the difference of σ_{22} and σ_{33} is nearly zero, so it may be considered taht $[-\partial P_z(r)/\partial \ln r]=\sigma_{11}-\sigma_{33}$. See references 1), 2) and 4).

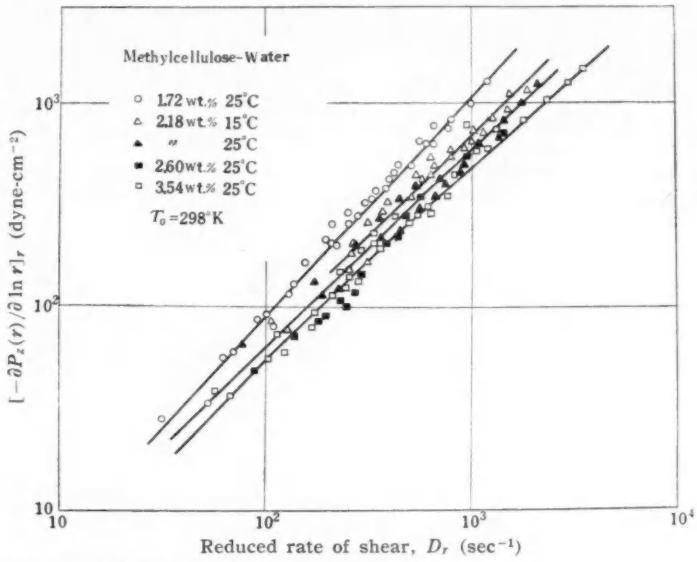

Fig. 5. Reduced normal pressure gradient, $[-\partial P_z(r)/\partial \ln r]_r = -[\partial P_z(r)/\partial \ln r][T_0/Tf(c)]$ vs. reduced rate of shear, $D_r = \eta_f T_0/Tf(c)$, where $f(c)=c$, T_0=298°K, solutions of methylcellulose in water.

have a distinct S shape[7], which indicates the presence of two different Newtonian regions at low rate of shear and at high rate of shear. In concentrated solutions the initial viscosity, $\eta_{D=0}$, at a low rate of shear increases more rapidly than the fifth or tenth power of the concentration[8], and the final viscosity, $\eta_{D=\infty}$, at a high rate of shear is proportional to the concentration itself[7]. These facts suggest that the whole feature of the flow curve can not be determined by their initial branch. This situation probably reflects also on the normal stresses, therefore, the above-mentioned superposition procedures should be valid only for the data obtained within the limited range of rates of shear and concentrations.

One more remark should be added to the factor T/T_0 of the shear modulus. This factor was derived from the conception of the entropy elasticity of the flexible chain polymer system. But in the case of concentrated solutions, in which the presence of transient junctions due to entanglements or interactions between polymer chains plays an important role and their number itself varies with temperature, the temperature dependence of the modulus of the solution is perhaps more complicated. A correct choice of this factor is a problem for further investigation.

7) J. G. Brodnyan, F. H. Gaskins and W. Philippoff, *Trans. Soc. Rheology*, **1**, 109 (1957).
8) T. G. Fox, S. Gratch and S. Loshaek, "Viscosity Relationships for Polymer in Bulk and in Concentrated Solutions", in Rheology, Vol. I ed. F. Eirich, Academic Press, New York (1956), Chap. 12.

Summary

Results of some geometrical studies of normal stress effects in a parallel plate instrument have been discussed. The parallelism and the concentricity of two plates are necessary conditions for the quantitative measurement. The rotational velocity of a cup should be kept below about 70 rpm for the apparatus with the cup radii about 6~8 cm. to avoid the influence of the centrifugal force. Accesses of manometer tubes with the diameter about 2 mm. cause no appreciable disturbances. The influence of side gap may also be neglected. With these experimental remarks, the normal stresses are obtained as a function of the rate of shear.

The applicability of the concentration-temperature superposition procedures has been tested with the data obtained here. They are partly valid in some limited range of variables.

A part of the measurement was performed by Mr. K. Sakamoto, to whom the authors express thanks. The authors are obliged to Professor T. Nakagawa of the University of Tokyo and Dr. M. Yamamoto of this University who attracted our attention to this problem. Thanks are also due to the members of the Research Group on Polymer Science of this University, especially to Professor H. Fujita for his helpful discussions on this problem. This work was supported by a grant-in-aid of the Ministry of Education and by Mitsubishi Paper Mills Co., Kyoto, to both of which we extend our thanks.

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Studies on the Sapogenins of Dioscorea tokoro Makino. I.[1]* *The Structure of Tokorogenic Acid*

By Katsura MORITA

(Received November 4, 1958)

Steroidal sapogenin from plants belonging to the family *Dioscoreaceae* in Japan was first reported in detail by Tsukamoto et al.[2] Nevertheless, until we reported the isolation of a new sapogenin from *Dioscorea tokoro* Makino, diosgenin had been the sole sapogenin from these plants. In a previous paper[1] we made clear the following points on the new sapogenin: (1) The elementary analyses of the sapogenin and its acetate coincide with those of trihydroxysapogenin and its triacetate. (2) The infrared absorption spectrum (980, 917, 895 and 862 cm^{-1}) shows that the sapogenin has iso-configuration of ring F[3]. (3) Chloroform solution of the sapogenin rapidly consumes bromine and evolves hydrogen bromide fume. (4) 16-Pregnene-x, y, z-triol-20-one triacetate, U.V.λ_{max}^{EtOH}: 240 mμ (ε: 1120), can be derived from the sapogenin by the isomerization to the pseudosapogenin followed by oxidation, hydrolysis and re-acetylation.

Since no trihydroxysapogenin possessing the same physical constants with this had so far been announced, we named this sapogenin "tokorogenin" and started to investigate its chemical structure.

Tokorogenin undergoes oxidation with chromic anhydride in acetic acid to give a dibasic acid "tokorogenic acid" and a small amount of a lactone-like substance, the structure of which has not yet been elucidated. Tokorogenin also undergoes oxidation with periodic acid in an ethanol solution giving a crystalline substance, $C_{34}H_{60}O_6$, which tends to become tokorogenic acid by treatment with aqueous acetic acid and subsequent oxidation with chromic anhydride in the same solvent. The I.R.-absorption spectrum of the periodic-acid oxidation product, however, showed that the substance possessed neither a hydroxyl group nor aldehyde functions, and therefore an acetal structure must be necessarily assigned to this substance.

Lead tetra-acetate also affects tokorogenin in 80% acetic acid, but no crystalline substance could be obtained. Quantitative estimation, however, showed that the oxidizing agent consumed in the reaction was almost equivalent to the value calculated for a glycerol structure.

In view of these results, it is quite reasonable to presume that tokorogenin possesses a glycerol moiety in ring A of steroid nucleus and that the chromic anhydride oxidation of this triol possibly causes elimination of one of its carbon atoms giving tokorogenic acid. It is, therefore, almost certain that tokorogenin must be defined as either spirostan-1, 2, 3-triol (I) or spirostan-2, 3, 4-triol (I') and

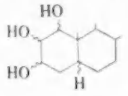
* This is a full paper of the previous communication (K. Morita, *Pharm. Bull.*, **5**, 496 (1957)), and constitutes Part VIII of Nishikawa's paper entitled "Studies in Steroids".

1) M. Nishikawa, K. Morita, H. Hagiwara and M. Inoue, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **74**, 1165 (1954).

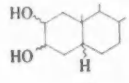
2) T. Tsukamoto and Y. Ueno, ibid., **56**, 802, 939 (1936).

3) C. R. Eddy et al., *Anal. Chem.*, **24**, 1337 (1952).

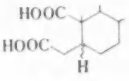
tokorogenic acid as either 1,3-seco-2-nor-spirostane-1,3-dioic acid (II) or 2,4-seco-3-nor-spirostane-2,4-dioic acid (II′).



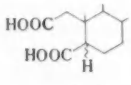
(I)



(I′)



(II)

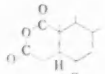
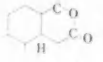


(II′)

These assumptions are further supported by the fact that tokorogenic acid, on heating with acetic anhydride, forms an anhydride (I.R. λ_{max}^{Nujol}: 5.51, 5.71 μ), for according to the Blanc rule[4] no seven-membered ring anhydride can be formed from the corresponding 1,6-dibasic acids under these conditions. Moreover, the elementary analytical values of tokorogenic acid, its dimethyl ester and the anhydride favor the values calculated for $C_{26}H_{40}O_6$, $C_{28}H_{44}O_6$ and $C_{26}H_{38}O_5$, respectively.

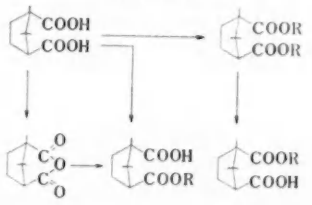
Evidence is also given by the fact that the infrared carbonyl bands of tokorogenic anhydride are typical of the 6-membered ring anhydride as shown in Table I.

TABLE I

Substance	Structure	I.R. max.	Ref. No.
Tokorogenic anhydride (III)		Nujol 5.55, 5.71	5)
3β-Acetoxy-5-etiobilienic anhydride		Nujol 5.55, 5.70	5)
Glutaric anhydride		$CHCl_3$ 5.55, 5.68	6)
Succinic anhydride		Nujol 5.36, 5.61	7)

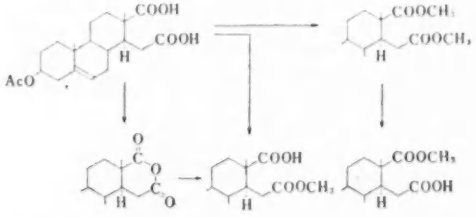
For the determination of the structure of tokorogenic acid, the following facts provide evidence in support of formula II rather than II′: (1) on treatment with methanol and hydrogen chloride tokorogenic acid affords a monomethyl ester (α-monomethyl ester); (2) alkaline hydrolysis of the dimethyl ester gives a different monomethyl ester (β-monomethylester); (3) treatment of the anhydride with one mole of sodium methoxide furnishes the α-monomethyl ester. These results are in complete accord with the earlier observations in the camphoric acid series (Chart 1)[8], where one of the carboxyl groups of the acid is attached to a tertiary carbon atom.

CHART 1



Since the structure II is closely similar to that of etiobilienic acid, which was first prepared from cholesterol by Kuwada[9] in our Laboratories, it can be presumed that etiobilienic acid and its derivatives will undergo reactions similar to those demonstrated in the camphoric acid series (Chart 1). We confirmed that this was true with etiobilienic acid, prepared from 5,16-pregnadien-3β-ol-20-one acetate according to Adams et al.[10]

CHART 2



On the basis of these findings and the aforementioned discussion, one is led to conclude that the reactions in the tokorogenic acid series can be best represented by Chart 3; that is, tokorogenic acid must have the structure II, and tokorogenic anhydride III, the α-monoester V, and the β-monoester VI, respectively.

4) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene", 3 Ed., Reinhold Publishing Corporation, New York, N. Y. (1949), p. 130.

5) Presented by the author.

6) H. H. Wasserman and H. E. Zimmerman, *J. Am. Chem. Soc.*, **72**, 5787 (1950).

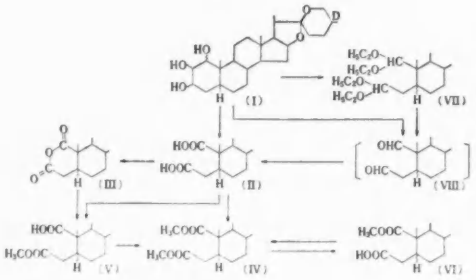
7) H. M. Randall et al., "Infra-red Determination of Organic Structure" D. Van Norstrand Co., Inc., New York, N. Y. (1949), p. 163.

8) J. W. Brühl, *Ber.*, **25**, 1796 (1892); W. A. Bone et al., *J. Chem. Soc.*, **85**, 534 (1904).

9) S. Kuwada, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **56**, 78 (1936).

It is also evident that the periodic acid oxidation product ($C_{34}H_{60}O_6$) must have a dialdehyde diacetal structure VII and that the structure I has to be assigned to tokorogenin.

CHART 3



Experimental

All melting points are corrected.

Tokorogenic Acid (II).— To a solution of 1.0 g. of tokorogenin I in 90 ml. of glacial acetic acid was added with vigorous stirring a solution of 2.0 g. of chromium trioxide in 20 ml. of 80% acetic acid at room temperature over a period of one hour. The solution was then allowed to stand overnight and the excess of the reagent was destroyed with sodium bisulfite. Partial evaporation gave a difficultly soluble crystalline substance of the solution (135 mg., m.p. 241°C (decomp.); I.R.λ_{max}^{Nujol}: 5.60 μ).

Anal. Found: C, 70.06; H, 8.74. Calcd. for $C_{27}H_{40}O_7$: C, 70.40; H, 8.75%.

The mother liquor was diluted with a large volume of water and extracted with ether, and the ethereal solution was repeatedly washed with water. The ethereal solution was then extracted with alkali and the alkaline solution was acidified and re-extracted with ether. Thorough washing of the solution followed by drying and evaporation furnished a solid residue (II, 470 mg.), which was recrystallized from acetic acid containing water yielding 400 mg. of colorless needles; m.p. 255°C (decomp.), $[\alpha]_D^{24}$ −26.3° (in acetone).

Anal. Found: C, 69.65; H, 9.13. Calcd. for $C_{26}H_{40}O_6$: C, 69.61; H, 8.99%.

Tokorogenic Acid Dimethyl Ester (IV).—A solution of tokorogenic acid II in ether was treated with a slight excess of diazomethane in the same solvent and the solution was immediately evaporated to dryness to give a crystalline dimethyl ester IV. Crystallization from methanol raised the melting point to 158～159°C.

Anal. Found: C, 70.75; H, 9.31. Calcd. for $C_{28}H_{44}O_6$: C, 70.55; H, 9.31%.

Tokorogenic Anhydride (III).—Tokorogenic acid II was heated with acetic anhydride for twenty minutes. After evaporation to a small volume the solution was cooled to give colorless needles of the anhydride III; m.p. 270～273°C, I.R.λ_{max}^{Nujol}: 5.55, 5.71 μ.

Anal. Found: C, 72.47; H, 9.09. Calcd. for $C_{26}H_{38}O_5$: C, 72.52; H, 8.90%.

A small portion of the anhydride III dissolved in methanol containing water and potassium hydroxide was digested for one hour, cooled, and neutralized with hydrochloric acid. Tokorogenic acid (II) was recovered in a good yield.

Tokorogenic Acid α-Monomethyl Ester (V).— a) To a mixture of 80 mg. of tokorogenic acid II and 3 ml. of absolute methanol was added 0.01 ml. of chlorosulfonic acid and the mixture was warmed on a steam bath to ensure complete solution. After being kept at room temperature for two hours the fine needles, which precipitated in the solution, were collected. Recrystallization from methanol afforded the analytical sample, which first melted at 141°C, then soon solidified and finally melted at 184～187°C (sintering 140°C).

Anal. Found: C, 69.88; H, 9.26. Calcd. for $C_{27}H_{42}O_6$: C, 70.10; H, 9.15%.

By the action of diazomethane V gave the dimethyl ester IV.

b) To a solution comprising 5 ml. of methanol and 6 mg. of sodium metal was added 100 mg. of the anhydride III and the mixture warmed on a steam bath for several minutes. The solution was then allowed to stand at room temperature for forty-five minutes. A small quantity of acetic acid was added to this and the solution was evaporated to dryness to give fine needles; m.p. 184～187°C (pre-sintering at 140°C). The sample here obtained did not show depression of melting point on admixture with a specimen prepared according to (a).

Tokorogenic Acid β-Monomethyl Ester (VI).—To a solution of 50 mg. of dimethyl ester IV in 4 ml. of methanol was added 100 mg. of sodium hydroxide dissolved in 1 ml. of water and the solution was refluxed for fifteen minutes on a steam bath and then allowed to stand at room temperature for one hour. The solution was diluted with a large volume of water, extracted with ether and the ethereal solution was discarded. After acidification, the aqueous layer was again extracted with ether and the ethereal solution was washed, dried and evaporated to give a solid substance VI. Recrystallization from methanol afforded colorless thin plates of the β-monomethyl ester VI; m.p. 208～210°C.

Anal. Found: C, 70.18; H, 9.04. Calcd. for $C_{27}H_{42}O_6$: C, 70.10, H, 9.15%.

By the action of diazomethane, the β-monomethyl ester VI gave the dimethyl ester IV melting at 158～159°C, which did not show depression of the melting point on admixture with the sample obtained by the other method.

Periodic Acid Oxidation of Tokorogenin (I).—To a suspension of 500 mg. of tokorogenin I in 10 ml. of absolute ethanol was added 1 g. of periodic acid dissolved in 1 ml. of water. The mixture was stirred vigorously for fifteen minutes and the resulting solution was allowed to stand

10) W. J. Adams et al., *J. Chem. Soc.*, **1956**, 297.

at room temperature for twenty-four hours to give colorless prisms. Recrytallization from methanol afforded 200 mg. of the diacetal VII; m.p. 150~151°C.

Anal. Found: C, 72.86; H, 10.55. Calcd. for $C_{34}H_{60}O_6$; C, 72.80; H, 10.71%.

Three hundred mg. of the diacetal dissolved in 80% acetic acid (40 ml.) was gently warmed on a steam bath for thirty minutes and cooled. To this was added a solution of 0.5 g. of chromic anhydride in 5 ml. of 80% acetic acid in small portions. Working up of the reaction mixture as in the case of tokorogenic acid II led to needles melting at 255°C; yield 190 mg., mixture m.p. with tokorogenic acid II, 255°C.

Lead Tetra-acetate Oxidation of Tokorogenin (I).—To a solution of lead tetra-acetate in 90% acetic acid (40 ml., 0.71 M) was added 444 mg. (1 mmol.) of tokorogenin I and the mixture was stirred vigorously to ensure complete solution. The solution was then allowed to stand at 20°C for two hours and a half. During this time, one ml. of the reaction mixture was taken out at regular intervals, a solution of potassium iodide was added to each of the solutions, and the solution was titrated with 0.1 N sodium thiosulfate with results shown in Table II, which show that tokorogenin consumed about two moles of the reagent.

TABLE II

Time	0.1N $Na_2S_2O_3$ ml.	HIO_4 Consumed m mol.
0 min.	0	0
15 min.	0.47	0.94
30 min.	0.67	1.34
45 min.	0.78	1.56
60 min.	0.81	1.62
90 min.	0.87	1.74
120 min.	0.91	1.82
16 hr.	1.21	2.42

3β-Hydroxy-Δ^5-etiobilienic Acid α-Monomethyl Ester.—a) A solution of 500 mg. of 3β-acetoxy-Δ^5-etiobilienic acid[9] in 30 ml. of methanol containing 0.5 ml. of chlorosulfonic acid was allowed to stand overnight at room temperature. After partial evaporation of the solution in vacuo water was added in small portions to give needles of the α-monomethyl ester. Recrystallization from acetone and water afforded the analytical sample melting at 175~178°C.

b) A solution of 350 mg. of 3β-acetoxy-Δ^5-etiobilienic anhydride[9] in 20 ml. of methanol containing 300 mg. of potassium hydroxide was refluxed on a steam bath for fifteen minutes. After standing at room temperature for thirty minutes a small quantity of acetic acid was added and the solution was evaporated in vacuo to a small volume. Water was added to this and the mixture was extracted with ether and the ethereal solution was extracted with alkali.

After acidification of the alkaline solution, it was extracted with ether, and then ethereal solution washed with water, dried and evaporated to give a syrup. Recrystallization from acetone and water afforded colorless needles melting at 175~178°C; mixed m. p. with the sample prepared according to (a), 175~178°C.

3β-Hydroxy-Δ^5-etiobilienic Acid β-Monomethyl Ester.—A solution of 500 mg. of 3β-acetoxy-Δ^5-etiobilienic acid dimethyl ester[10] in 30 ml. of methanol containing 300 mg. of patassium hydroxide was refluxed on a steam bath for four hours. After evaporation in vacuo a large volume of water was added to this and the mixture was extracted with ether. From the ether solution, 200 mg. of the material melting at 110~112°C was recovered. The aqueous solution, after acidification with diluted hydrochloric acid, was extracted with ether, and the ethereal solution was washed with water, dried and evaporated to give fine needles melting at 214~215°C*.

The β-monomethyl ester, on treatment with diazomethane, gave the dimethyl ester.

Summary

(1) Oxidation of tokorogenin by means of chromic anhydride in acetic acid, periodic acid in ethanol and lead tetra-acetate in aqueous acetic acid led to the conclusion that tokorogenin must have a glycerol moiety in ring A of the steroid nucleus.

(2) Tokorogenic acid, an oxidation product from tokorogenin, forms an anhydride by heating with acetic anhydride and gives rise to a monomethyl ester (α-monoester) by treatment with methanol and hydrogen chloride, while alkaline hydrolysis of the dimethyl ester of the acid furnishes a different monomethyl ester (β-monoester). The same α-monoester also results from tokorogenic anhydride by the action of alkali in a methanol solution.

(3) On the basis of the theoretical considerations and the afore-mentioned observations in the tokorogenic acid series compared with those in the camphoric acid and etiobilienic acid series, it is concluded that tokorogenic acid has to be defined as 1,3-seco-2-nor-spirostan-1,3-dioic acid (II) and hence tokorogenin as spirostan-1,2,3-triol (I).

The author wishes to express his grateful thanks to Dr. Y. Asahina of the University of Tokyo, Dr. S. Kuwada and Dr. T. Matsukawa in our Research Laboratories for their encouragement throughout the work. Thanks are also due to Mr. H. Kamio

* Kuwada[9] assigned the m. p. 176~177°C (sinter. at 165°C) to the same monomethyl ester. Discrepancy between the melting points may would be attributed to the solvents ethanol being used by Kuwada.

for infrared- and ultraviolet-spectral measurements and to Mr. M. Kan for elementary analyses.

Takeda Research Laboratories, Juso, Higashiyodogawa-ku, Osaka

Phenothiazine Derivatives. VI[1]*. Reactions of Some Substituted Phenothiazines with Thionyl Chloride*

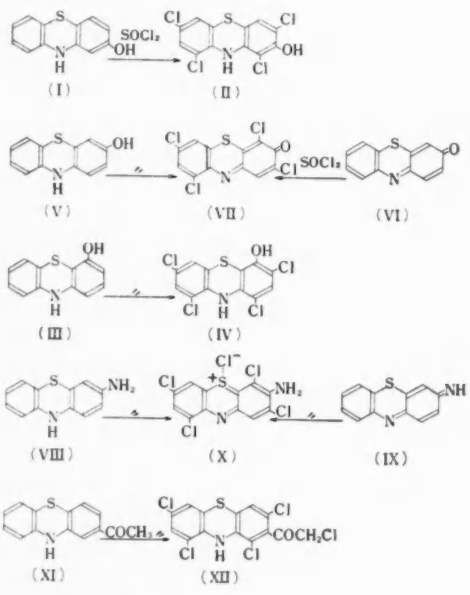
By Manabu FUJIMOTO

(Received October 9, 1958)

In Part II[2] of the present series, it was reported that thionyl chloride transforms phenothiazine and its 5-oxide into 1,3,7,9-tetrachlorophenothiazine. Besides the present series, two reports have been published on the nuclear substitutions of phenothiazine derivatives with thionyl chloride. Namely, phenothiazine-1-carboxylic acid gave 3,7,9-trichlorophenothiazine-1-carbonyl chloride[3], and phenothiazine-2-carboxylic acid 1,3,7,9-tetrachlorophenothiazine-2-carbonyl chloride[4].

The present paper describes similar substitution reactions of some other phenothiazine derivatives with thionyl chloride.

CHART I



Mono-substituted Phenothiazines. — As shown in Chart I, the action of thionyl chloride gave 1,3,7,9-tetrachloro-2-hydroxyphenothiazine (II) from 2-hydroxyphenothiazine (I), 2,4,7,9-tetrachloro-3-phenothiazone (VII) from 3-hydroxyphenothiazine (V) and from 3-phenothiazone (VI), and 3-amino-2,4,7,9-tetrachlorophenazathionium chloride (X) from 3-aminophenothiazine (VIII) and from 3-phenothiazime (IX). These three products, II, VII and X, had been obtained by the action of thionyl chloride on 3-hydroxydiphenylamine, 4-hydroxydiphenylamine and 4-aminodiphenylamine, respectively[5]. In Part III[6] of this series it was observed that the reaction of thionyl chloride with diphenylamine to form 1,3,7,9-tetrachlorophenothiazine proceeds through the intermediate formation of phenazathionium chloride and subsequent chlorination. The fact that the substituted phenothiazines and the corresponding diphenylamines gave the same products by the action of thionyl chloride affords support to the above mechanism of the reaction of thionyl chloride with diphenylamine. Thionyl chloride and 4-hydroxyphenothiazine (III) gave a new tetrachloro-4-hydroxyphenothiazine. As it is expected that the hydroxyl group in position 4 of 4-hydroxyphenothiazine will strengthen the 1,3-orienting effect by the imino group, the

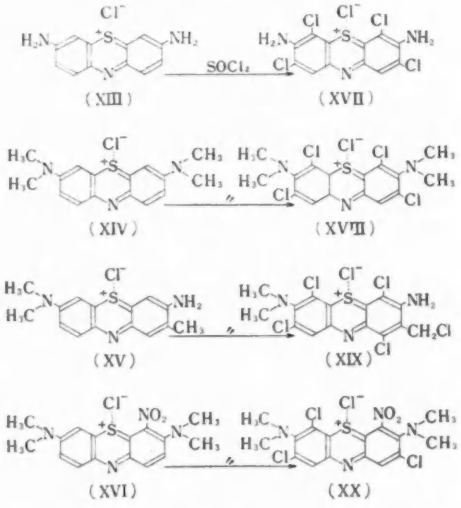
1) Part V: This Bulletin, **32**, 371 (1959).
2) *Pharm. Bull. (Japan)*, **5**, 393 (1957).
3) N. V. Savitskaya and M. N. Shahukina, *Zhur. Obshchei Khim.*, **24**, 152 (1954).
4) A. Burger and J. B. Clements, *J. Org. Chem.*, **19**, 1113 (1954).
5) This Bulletin, **32**, 298 (1959).
6) Ibid., **32**, 294 (1959).

product is assumed with great certainty to be 1,3,7,9-tetrachloro-4-hydroxyphenothiazine (IV).

2-Acetylphenothiazine (XI) gave a pentachloro derivative. A part of the chlorine atoms was found labile giving easily the chloride anion, and thus was present in the side chain. The positions of the chlorine atoms in the ring with the chlorinated acetyl group can not be presumed unequivocally, because the orienting effect by the acetyl group and that by the imino group do not fall on the same positions, but the product can be assumed to be 1,3,7,9-tetrachloro-2-(chloroacetyl)-phenothiazine (XII) in analogy to 1,3,7,9-tetrachlorophenothiazine-2-carbonyl chloride from phenothiazine-2-carboxylic acid[4].

Phenothiazine Dyes[7]. — From among many known phenothiazine dyes, thionine (XIII), methylene blue (XIV), toluidine blue (XV) and methylene green B (XVI) were chosen for the reactions with thionyl chloride.

CHART II



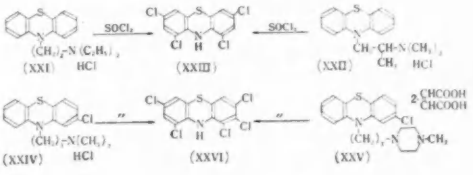
In the order of mention, they gave 3,7-diamino-2,4,6,8-tetrachlorophenazathionium chloride (XVII), 3,7-bis(dimethylamino)-2,4,6,8-tetrachlorophenazathionium chloride (XVIII), 3-amino-1,4,6,8-tetrachloro-2-(chloromethyl)-7-(dimethylamino)-phenazathionium chloride (XIX), and 2,6,8-trichloro-3,7-bis(dimethylamino)-4-nitrophenazathionium chloride (XX), respectively.

7) These dyes are expediently expressed in phenazathionium formulae.

As it is reasonably expected that the amino group and the dimethylamino group in positions 3 and 7 are stronger in the orienting effect than the competing nitrogen atom of position 10, substitution took place presumably in all the positions 2,4,6 and 8, unless already substituted. Toluidine blue (XV) gave a pentachloro derivative. It can be assumed by the same reason as stated above that three of the five chlorine atoms are situated at positions 4, 6, and 8. As substitution in position 1 is favored by both the nitrogen atom of position 10 and the methyl group in position 2, one is probably in position 1, and the remaining one in the methyl group to make chloromethyl group. Thus the pentachloro product is considered 3-amino-1,4,6,8-tetrachloro-2-(chloromethyl)-7-(dimethylamino)phenazathionium chloride (XIX).

Phenothiazine Drugs.—Four of the most important phenothiazine drugs were treated with thionyl chloride with results shown in Chart III. The same 1,3,7,9-tetrachlorophenothiazine (XXIII)[2] was obtained from either diethazine (XXI) (2987 R.P.) or promethazine (XXII) (3389 R.P.). In a similar manner, 1,2,3,7,9-pentachlorophenothiazine[2] (XXVI) was derived from chlorpromazine (XXIV) (4560 R.P.) and from prochlorperazine

CHART III



(XXV) (6140 R.P.). As the yields were nearly quantitative, the reaction with thionyl chloride may be useful to the qualitative and quantitative analyses of various phenothiazine drugs.

Experimental

General Procedure of Treatment with Thionyl Chloride.— Thionyl chloride (10 ml.) was added dropwise to 1.0 g. of the compound to be treated, and the mixture was heated gently under reflux for 30 min., when hydrogen chloride and sulfur dioxide were evolved. The cooled mixture was poured onto crushed ice, and the product was collected, dried, and recrystallized.

1,3,7,9-Tetrachloro-2-hydroxyphenothiazine (II) from 2-Hydroxyphenothiazine (I). —Fine powder of chocolate color from chloroform-ethanol, m.p. 202~203°C (decomp.). Yield,

93%. The substance was identified with an authentic sample[5].

1,3,7,9-Tetrachloro-4-hydroxyphenothiazine (IV) from 4-Hydroxyphenothiazine (III).—Fine powder with chocolate color from benzene, m.p. 168~170°C. Yield, 94%. The product IV gives bluish-violet color with sulfuric acid.

Anal. Found: C, 40.67; H, 1.10; N, 4.01. Calcd. for $C_{12}H_5ONCl_4S$: C, 40.82; H, 1.43; N, 3.97%.

2,4,7,9-Tetrachloro-3-phenothiazone (VII) from 3-Hydroxyphenothiazine (V) and from 3-Phenothiazone (VI).—Fine crystals with pinkish tinge from ethanol-benzene, m.p. 145~146°C. Yields, 92% from V and 97% from VI. The product VII gives cobalt-blue coloration with sulfuric acid. The substance showed no depression of the melting point on admixture with an authentic sample[5].

3-Amino-2,4,7,9-tetrachlorophenazathionium Chloride (X) from 3-Aminophenothiazine (VIII) and from 3-Phenothiazime (IX).—Reddish-violet fine powder from chloroform, m.p. 185~186°C. Yields, 89% from VIII and 99% from IX. The substance showed no depression of the melting point on admixture with an authentic sample[5].

1,3,7,9-Tetrachloro-2-(chloroacetyl)phenothiazine (XII) from 2-Acetylphenothiazine (XI).—Green powder, m.p. 145~146°C. Yield, quantitative. Coloration with sulfuric acid is violet. Silver chloride was precipitated on adding silver nitrate to an alcoholic solution of the substance XII.

Anal. Found: C, 37.19; H, 1.93; N, 3.15. Calcd. for $C_{14}H_6ONCl_5S \cdot 2H_2O$: C, 37.37; H, 2.24; N, 3.11%.

3,7-Diamino-2,4,6,8-tetrachlorophenazathionium Chloride (XVII) from Thionine (XIII).—Bluish-purple fine powder from methanol, m.p. over 360°C. Yield, 99%. The substance gives dark green color with sulfuric acid.

Anal. Found: C, 35.99; H, 1.83; N, 10.54. Calcd. for $C_{12}H_6N_3Cl_5S$: C, 35.90; H, 1.51; N, 10.47%.

2,4,6,8-Tetrachloro-3,7-bis(dimethylamino)-phenazathionium Chloride (XVIII) from Methylene Blue (XIV).—Greenish-blue fine crystals, m.p. over 360°C. Yield, 94%. The substance gives green color with sulfuric acid. When recrystallized from a mixture of dimethylformamide and water, it was transformed into the corresponding phenazathionium hydroxide, which was analyzed.

Anal. Found: C, 43.66; H, 3.28; N, 10.06. Calcd. for $C_{16}H_{13}ON_3Cl_4S$: C, 43.75; H, 3.44; N, 9.57%.

3-Amino-1,4,6,8-tetrachloro-2-(chloromethyl)-7-(dimethylamino)phenazathionium Chloride (XIX) from Toluidine Blue (XV).—Purplish-blue fine powder from acetic acid, m.p. over 360°C. Yield, 96%. It gives reddish-brown color with sulfuric acid.

Anal. Found: C, 37.90; H, 2.72; N, 8.48. Calcd. for $C_{15}H_{11}N_3Cl_6S$: C, 37.68; H, 2.32; N, 8.79%.

2,6,8-Trichloro-3,7-bis(dimethylamino)-4-nitrophenazathionium Chloride (XX) from Methylene Green B (XVI).—Green fine powder from methanol, m.p. 234~237°C (decomp.). Yield, quantitative. Coloration with sulfuric acid is violet.

Anal. Found: C, 40.88; H, 3.40; N, 12.09. Calcd. for $C_{16}H_{14}O_2N_4Cl_4S$: C, 41.05; H, 3.01; N, 11.97%.

1,3,7,9-Tetrachlorophenothiazine (XXI) from Diethazine (XIX) and from Promethazine (XX).—Yellow needles from benzene, m.p. 234~235°C. Yields, 99% from XIX and 96% from XX. It was identified with an authentic sample[2].

1,2,3,7,9-Pentachlorophenothiazine (XXVI) from Chlorpromazine (XXIV) and from Prochlorperazine (XXV).—Faint-yellow or colorless needles from benzene, m.p. 204~205°C. Yields, 96% from XXIV and 90% from XXV. It was identified with an authentic sample[2].

Summary

Some phenothiazine derivatives including dyes and drugs were treated with thionyl chloride and five new polychlorinated products and six known were obtained.

The author expresses his thanks to Professor Y. Urushibara, the Tokyo, for his helpful guidance throughout this work, to Dr. K. Takeda, Director of the Laboratory, for his permission to conduct this research, and also to the members of the Center of Microanalytical Services, Shionogi and Co., Ltd., for the elementary analyses.

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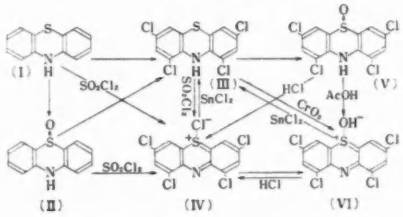
Phenothiazine Derivatives. VII[1]. *Reactions of Phenothiazines with Sulfuryl Chloride and with Chlorosulfonic Acid*

By Manabu FUJIMOTO

(Received October 9, 1958)

In the previous papers of this series, reactions of diphenylamines and phenothiazines with thionyl halides, and of diphenylamine with sulfuryl chloride were described[2]. The present paper deals with the reactions of phenothiazines with sulfuryl chloride and with chlorosulfonic acid.

CHART I



The action of sulfuryl chloride on phenothiazine (I), on phenothiazine 5-oxide (II), and on 1,3,7,9-tetrachlorophenothiazine (III) produced chocolate-colored mixtures which, on treatment with water, gave a highly chlorinated product. The molecular weight of the purified product was found to be 309, and it was analyzed as $C_{12}H_5ONCl_4S$, corresponding to 1,3,7,9-tetrachlorophenazathionium hydroxide (VI).

Brady and Smiles[3] obtained 1,3,7,9-tetrachlorophenazathionium hydroxide(VI) by treating 1,3,7,9-tetrachlorophenothiazine 5-oxide (V) with aqueous sulfuric acid, and they described the substance as a brownish-red powder, decomposing somewhat gradually at 200°C and giving a purple solution in sulfuric acid. The substance obtained by the present author is a fine powder of chocolate color melting at 210~211°C (decomp.) and giving violet coloration with sulfuric acid. We may well be justified in regarding the present substance as identical with the substance of Brady and Smiles.

Without treatment with water, 1,3,7,9-tetrachlorophenazathionium chloride (IV) was obtained as the precursor of the hydroxide VI. Hydrolysis of the purified chloride IV with aqueous sulfuric acid or with ethanolic potassium hydroxide gave the phenazathionium hydroxide VI. Therefore, it was concluded that the treatment of the primary reaction mixtures with water caused a hydrolysis by sulfuric acid which was generated from water and the remaining sulfuryl chloride.

Mutual transformations of the four 1,3,7,9-tetrachlorophenothiazine derivatives, III, IV, V and VI, were further investigated. Reduction of 1,3,7,9-tetrachlorophenathionium chloride (IV) and of the hydroxide VI with stannous chloride gave 1,3,7,9-tetrachlorophenothiazine (III), while the hydroxide VI was produced either by oxidation of the phenothiazine III with chromic anhydride in benzene or by intramolecular rearrangement of 1,3,7,9-tetrachlorophenothiazine 5-oxide (V) in acetic acid. Action of dry hydrogen chloride on the 5-oxide (V) and on the

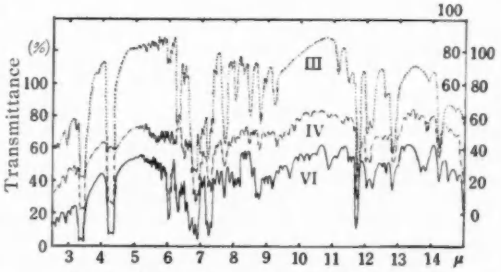


Fig. 1. Infrared spectra in Nujol of 1,3,7,9-tetrachlorophenothiazine (III), 1,3,7,9-tetrachlorophenazathionium chloride (IV), and the hydroxide VI.

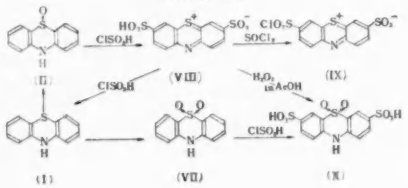
phenazathionium hydroxide VI yielded the phenazathionium chloride IV. These transformations demonstrate that the four chlorine atoms are situated at the corresponding positions in the four compounds concerned. The infrared absorptions of

1) Part VI, This Bulletin, **32**, 480 (1959).
2) Part II, *Pharm. Bull.* (*Japan*), **5**, 395 (1957); Part III, IV and VI, This Bulletin, **32**, 294, 296, 480 (1959).
3) O. L. Brady and S. Smiles, *J. Chem. Soc.*, **97**, 1562 (1910).

three (III, IV and VI) of the four compounds also indicate that they are similarly substituted (Fig. 1).

Phenothiazine 5,5-dioxide (VII) did not react with sulfuryl chloride, but chlorosulfonic acid transformed it into a disulfonic acid, probably 3,7-disulfophenothiazine 5,5-dioxide (X), as shown in Chart II.

CHART II



The action of chlorosulfonic acid on phenothiazine (I) and on its 5-oxide (II) gave an inner salt VIII of 3,7-disulfophenazathionium hydroxide. The inner salt VIII has converted into the disulfonic acid X by oxidation with 30% hydrogen peroxide in acetic acid, and into the inner salt IX of 3-sulfo-7-(chlorosulfonyl)phenazathionium hydroxide on treatment with thionyl chloride. Thus the sulfo groups and the chlorosulfonyl group in these inner salts are situated at the same positions as in the disulfophenothiazine 5,5-dioxide (X), which were assumed to be 3 and 7 as mentioned above.

Experimental

Reduction of 1,3,7,9-Tetrachlorophenazathionium Chloride (IV) and of 1,3,7,9-Tetrachlorophenazathionium Hydroxide (VI) with Stannous Chloride. — a) A mixture of 1.0 g. of 1,3,7,9-tetrachlorophenazathionium chloride (IV), described below, and 0.8 g. of stannous chloride was dissolved in 20 ml. of acetic acid, and then 1.0 g. of 35% hydrochloric acid was added. The solution was refluxed during 3 hr., and the cooled mass was poured into water. The yellow precipitate was collected, dried, and recrystallized from dioxane. Yellow needles, m. p. 235~236°C. Yield, 96%. The substance was identified with 1,3,7,9-tetrachlorophenothiazine (III) by a mixed melting point determination with an authentic sample[2].

b) Similarly, 1,3,7,9-tetrachlorophenazathionium hydroxide (VI), described below, gave the same tetrachlorophenothiazine (III) in a yield of 94%.

1,3,7,9-Tetrachlorophenazathionium Chloride (IV). — a) Sulfuryl chloride (10 ml.) was added to 1.0 g. of phenothiazine (I), and the mixture was gently refluxed for 30 min. Then the excess of sulfuryl chloride was evaporated under reduced pressure. The product was recrystallized from benzene. 1,3,7,9-Tetrachlorophenazathionium chloride (IV) was obtained in chocolate-colored needles, m. p. 223~224°C (decomp.). Yield, nearly quantitative. It gives purple coloration with sulfuric acid.

Anal. Found: C, 38.95; H, 1.43; N, 3.98. Calcd. for $C_{12}H_4NCl_5S$: C, 38.79; H, 1.09; N, 3.77%.

On treatment with sulfuryl chloride in a similar manner, phenothiazine 5-oxide (II) and 1,3,7,9-tetrachlorophenothiazine (III) gave the same product IV also in nearly quantitative yields.

b) A carbon tetrachloride solution of 1,3,7,9-tetrachlorophenothiazine 5-oxide (V) was saturated with dry hydrogen chloride, the chocolate-colored solution was refluxed for 1 hr., and then the solvent was distilled off. The residue was recrystallized from benzene. 1,3,7,9-Tetrachlorophenazathionium chloride (IV) was obtained quantitatively.

1,3,7,9-Tetrachlorophenazathionium Hydroxide (VI).—a) The reaction mixture resulting from phenothiazine (I) and sulfuryl chloride as described above, was poured into water, and the chocolate-colored product was collected, dried and recrystallized from benzene. 1,3,7,9-Tetrachlorophenazathionium hydroxide (VI) was obtained in chocolate-colored needles, m. p. 210~211°C. Yield, quantitative. It gives violet coloration with sulfuric acid.

Anal. Found: C, 40.49; H, 1.54; N, 4.03; mol. wt. (Rast), 309. Calcd. for $C_{12}H_5ONCl_4S$: C, 40.82; H, 1.43; N, 3.97%; mol. wt., 353.

b) 1,3,7,9-Tetrachlorophenazathionium chloride (IV) (0.2 g.) was dissolved in 5 ml. of sulfuric acid, and then the mixture was poured into 50 ml. of water. A nearly quantitative yield of the same hydroxide VI was obtained.

c) The chloride IV (0.2 g.) was dissolved in 50 ml. of hot ethanol, and a solution of 0.1 g. of potassium hydroxide in 5 ml. of hot ethanol was added. After reflux during 1 hr., the solvent was distilled off, and then the residue was neutralized with 10% hydrochloric acid. Recrystallization of the insoluble part from benzene gave 1,3,7,9-tetrachlorophenazathionium hydroxide (VI).

d) To a solution of 1.0 g. of 1,3,7,9-tetrachlorophenothiazine (III) in 50 ml. of benzene, 1.0 g. of chromic anhydride was added little by little. The mixture was refluxed on a water bath during 3 hr. The solvent was distilled off, and the residue was poured onto crushed ice. The same hydroxide VI was obtained in a quantitative yield.

e) A solution of 1.0 g. of 1,3,7,9-tetrachlorophenothiazine 5-oxide (V) in 30 ml. of acetic acid was refluxed for 1 hr., and the chocolate-colored solution was evaporated in vacuo. The residue was recrystallized from benzene, and 1,3,7,9-tetrachlorophenazathionium hydroxide (VI) was obtained in chocolate-colored fine needles.

Inner Salt VIII of 3,7-Disulfophenazathionium Hydroxide. — Chlorosulfonic acid (10 ml.) was added dropwise to phenothiazine (I),

and the mixture was heated gently under reflux for 30 min., and then the cooled mass was poured onto crushed ice. The precipitate was collected, dried, and recrystallized from benzene. The inner salt VIII of 3,7-disulfophenazathionium hydroxide was obtained in dark reddish-violet powder, m.p. 225~226°C. Yield, 93%. It gives bluish-violet coloration with sulfuric acid.

Anal. Found: C, 36.56; H, 2.39; N, 3.85. Calcd. for $C_{12}H_7O_6NS_3 \cdot 2H_2O$: C, 36.64; H, 2.82; N, 3.56%.

Treatment of phenothiazine 5-oxide (II) with chlorosulfonic acid in a similar manner gave the same product in a yield of 97%.

Inner Salt IX of 3-Sulfo-7-(chlorosulfonyl)phenazathionium Hydroxide.—Thionyl chloride (10 ml.) was added drop by drop to 1.0 g. of the inner salt VIII of 3,7-disulfophenazathionium hydroxide, when hydrogen chloride and sulfur dioxide was evolved. After reflux during 30 min., the mixture was poured into water. The precipitate was collected, dried, and recrystallized from ethyl acetate. The inner salt IX of 3-sulfo-7-(chlorosulfonyl)phenazathionium hydroxide was obtained in dark-violet powder, m.p. 163~164°C. Yield, 0.9 g. (94%). It gives cobalt-blue coloration with sulfuric acid.

Anal. Found: C, 38.70; H, 1.80; N, 3.66. Calcd. for $C_{12}H_6O_5NClS_3$: C, 38.35; H, 1.61; N, 3.73%.

3,7-Disulfophenothiazine 5,5-Dioxide (X).—a) The reaction of phenothiazine 5,5-dioxide (VII) and sulfuryl chloride gave 3,7-disulfophenothiazine 5,5-dioxide (X) as a hygroscopic, dark-green substance. Yield, over 86% of the theory. The substance X is soluble in water, in ethanol, and in methanol. The sodium, potassium, calcium and barium salts are easily soluble in water. Coloration with sulfuric acid is reddish-purple.

b) To a solution of substance VIII in 40 ml. of acetic acid, 1.0 ml. of 30% hydrogen peroxide was added, and the solution was heated on a water bath during 3 hr. Evaporation of the solvent gave the same disulfonic acid X. Yield of the crude product, quantitative.

Summary

Reactions of some phenothiazines with sulfuryl chloride and with chlorosulfonic acid were investigated. With sulfuryl chloride, phenothiazine (I), its 5-oxide (II), and 1,3,7,9-tetrachlorophenothiazine (III) gave the same product, 1,3,7,9-tetrachlorophenazathionium chloride (IV), which yielded the corresponding hydroxide VI by the action of aqueous sulfuric acid and of ethanolic potassium hydroxide. To establish the structural relationship of these substances, mutual transformations were carried out. Treatment of phenothiazine and of its 5-oxide with chlorosulfonic acid gave the inner salt VIII of 3,7-disulfophenazathionium hydroxide, which yielded the inner salt IX of 3-sulfo-7-(chlorosulfonyl)phenazathionium hydroxide by the action of thionyl chloride. Chlorosulfonic acid converted phenothiazine 5,5-dioxide into 3,7-disulfophenothiazine 5,5-dioxide which was obtained also by the oxidation of the inner salt VIII with 30% hydrogen peroxide in acetic acid.

The author expresses his thanks to Professor Y. Urushibara, the University of Tokyo, for his helpful guidance throughout this work, to Dr. K. Takeda, Director of the Laboratory, for his permission to conduct this research, and also to the members of the Center of Microanalytical Services, Shionogi and Co., Ltd., for the elementary analyses and the infrared spectal measurements.

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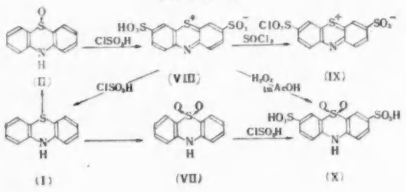
three (III, IV and VI) of the four compounds also indicate that they are similarly substituted (Fig. 1).

Phenothiazine 5,5-dioxide (VII) did not react with sulfuryl chloride, but chlorosulfonic acid transformed it into a disulfonic acid, probably 3,7-disulfophenothiazine 5,5-dioxide (X), as shown in Chart II.

CHART II



The action of chlorosulfonic acid on phenothiazine (I) and on its 5-oxide (II) gave an inner salt VIII of 3,7-disulfophenazathionium hydroxide. The inner salt VIII has converted into the disulfonic acid X by oxidation with 30% hydrogen peroxide in acetic acid, and into the inner salt IX of 3-sulfo-7-(chlorosulfonyl)phenazathionium hydroxide on treatment with thionyl chloride. Thus the sulfo groups and the chlorosulfonyl group in these inner salts are situated at the same positions as in the disulfophenothiazine 5,5-dioxide (X), which were assumed to be 3 and 7 as mentioned above.

Experimental

Reduction of 1,3,7,9-Tetrachlorophenazathionium Chloride (IV) and of 1,3,7,9-Tetrachlorophenazathionium Hydroxide (VI) with Stannous Chloride. — a) A mixture of 1.0 g. of 1,3,7,9-tetrachlorophenazathionium chloride (IV), described below, and 0.8 g. of stannous chloride was dissolved in 20 ml. of acetic acid, and then 1.0 g. of 35% hydrochloric acid was added. The solution was refluxed during 3 hr., and the cooled mass was poured into water. The yellow precipitate was collected, dried, and recrystallized from dioxane. Yellow needles, m. p. 235~236°C. Yield, 96%. The substance was identified with 1,3,7,9-tetrachlorophenothiazine (III) by a mixed melting point determination with an authentic sample[2].

b) Similarly, 1,3,7,9-tetrachlorophenazathionium hydroxide (VI), described below, gave the same tetrachlorophenothiazine (III) in a yield of 94%.

1,3,7,9-Tetrachlorophenazathionium Chloride (IV). — a) Sulfuryl chloride (10 ml.) was added to 1.0 g. of phenothiazine (I), and the mixture was gently refluxed for 30 min. Then the excess of sulfuryl chloride was evaporated under reduced pressure. The product was recrystallized from benzene. 1,3,7,9-Tetrachlorophenazathionium chloride (IV) was obtained in chocolate-colored needles, m. p. 223~224°C (decomp.). Yield, nearly quantitative. It gives purple coloration with sulfuric acid.

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b) A carbon tetrachloride solution of 1,3,7,9-tetrachlorophenothiazine 5-oxide (V) was saturated with dry hydrogen chloride, the chocolate-colored solution was refluxed for 1 hr., and then the solvent was distilled off. The residue was recrystallized from benzene. 1,3,7,9-Tetrachlorophenazathionium chloride (IV) was obtained quantitatively.

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Analysis of Organic Compounds by Flame Spectrometry. I. Determination of Chlorine in Organic Compounds by Band Spectra of Cuprous Chloride*

By Masao MARUYAMA and Setsuya SENO

(Received September 1, 1958)

Analysis by flame spectrometric method has developed around metal elements with low excitation energy and recently its application has gradually been extended to heavy metals. On the other hand, determination of nonmetallic elements has been reported only in a few instances, such as the determination of phosphorus[1] and halogen[2] by indirect method, that of the chloride ion in sea water by band spectrum of cuprous chloride[3], that of organophosphorus compounds[4], and semiquantitative determination of the fluoride ion by photographic measurement[5].

The present writers re-examined the determination of the chloride ion by the band spectrum of cuprous chloride, based on the so-called Beilstein's reaction, developed by Honma and others[3].

It was thereby learned that a stable band spectrum of cuprous chloride can be obtained similarly even in the case of non-ionized chloride and a rapid determination of chlorine in organic compounds was carried out successfully by the use of an organic solvent, *N*, *N*-dimethylformamide (DMF).

Experimental

Apparatus and Reagents.—Measurement of flame spectrum was made with Beckman Model DU spectrophotometer (with 4300 photomultiplier accessory), with 9200 flame attachment, 4020 atomizer burner, and 92300 spectral energy recording adapter. Hydrogen and oxygen were used for excitation. To obtain a stable low pressure hydrogen flow, a combination of a flow meter, a hydraulic pressure governor, and a damper was placed between the burner and the gas regulator. Brief outline of this apparatus is shown in Fig. 1.

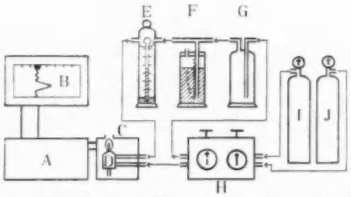

Fig. 1. Schematic diagram of the apparatus.

A Beckman DU spectrophotometer
B Spectral energy recording adapter
C Flame attachment
D Atomizer burner
E Flow meter
F Hydraulic pressure governor
G Damper
H Fuel pressure regulator
I Hydrogen cylinder
J Oxygen cylinder

The reagents used were all commercial reagents of special grade (G.R. grade). The solvent, DMF was dehydrated and distilled, collecting the fraction of b.p. 152~153°C. Standard substance for chloride was the γ-isomer of BHC (hexachlorocyclohexane) of standard quality for polarographic analysis.

Experimental Procedure.—*Preparation of the solvent* (Cu, 0.05 M).—In dehydrated DMF, 12.08 g. of cupric nitrate (trihydrate) was dissolved and 1 cc. of nitric acid was added into this solution to prevent the precipitation of cupric hydroxide or basic cupric chloride and the solution was brought up to 1000 cc.

Preparation of standard chloride solution and sample solution.—In a 100 cc. volumetric flask, 4.848 g. of standard BHC (chloride equivalent, 48.48) was accurately weighed and dissolved in DMF containing 0.05 M of copper to prepare standard 1 M chloride solution. The solution was diluted as required to a concentration of 0.05~0.1 M chloride. Test solutions were prepared by placing a quantity of the sample corresponding to 0.2~1.0 mM of chloride in a 20 cc. volumetric flask and dissolved in DMF containing copper.

Procedure of flame photometric analysis.—For the analysis, a peak of the band spectrum of cuprous chloride at 435.4 mμ was used and the calibration curve was made from the height of the base line to the peak of the spectral curve.

1) W. A. Dippel, C. E. Bricker and N. F. Furman, *Anal. Chem.*, **26**, 553 (1954).
2) O. Menis, H. P. House and T. C. Rains, ibid., **29**, 76 (1957).
3) M. Honma, ibid., **27**, 1656 (1955).
4) O. W. Brite, ibid., **27**, 1815 (1955).
5) R. Ishida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 241 (1956).

* The gist of this work was presented at the 6th Annual Meeting of the Japan Society for Analytical Chemistry in October, 1957.

Conditions of the measurement were as follows: wavelength, 442 to 428 mμ; slit width, 0.05 mm.; sensitivity, full; oxygen pressure, 1.76 kg./cm² (25 lb./in²) on the fuel pressure gauge; hydrogen pressure, 1st, 0.035 kg./cm² (0.5 lb./in²) on the fuel pressure gauge, 2nd, 10 cm. water column; hydrogen flow rate, 450 cc./min.; scanning speed, 10, on the scale of the instrument; chart speed, 7.62 cm./min. (3 in./min.).

Experimental Results and Discussion

Exeitation of Cuprous Chloride Band Spectrum.—The band spectrum of cuprous chloride emitted in oxy-hydrogen flame has bands at the wave lengths listed in Table I[6].

TABLE I. BAND SPECTRA OF CUPROUS CHLORIDE

Wavelength (mμ)	Relative intensity	Wavelength (mμ)	Relative intensity
526.2_3	6	443.3_8	9
498.2_2	2	441.2_4	8
494.6_2	1	435.3_9	10
488.1_5	4	433.3_2	9
484.6_4	3	428.0_9	9
478.8_5	2	425.8_9	7
475.5_7	1	418.7_9	3
449.3_8	5		

The brightest of these is the band at 435.4 mμ, followed by bands at 443.4, 433.3 and 428.1 mμ; 435.4 mμ was taken as the analytical wavelength.

Honma and others have already examined the cuprous chloride band spectrum of a sample in aqueous solution and found that its measured intensity is low and the slit width must be so wide that hardly any fine structures were observed. It was also pointed out that, in this wavelength region, the cuprous chloride band spectrum is interfered by C_2-Swan band owing to the presence of carbon compounds, and does not make quantitative estimation possible.

The present writers, however, were able to overcome these difficulties by weakening the interfering action of C_2-Swan band by careful adjustment of the fuel gas pressure even in the presence of organic compounds and by markedly increasing the intensity of cuprous chloride band spectrum by the use of a suitable organic solvent in place of water.

In general, organic compounds are sparingly soluble in water and the use of an organic solvent will be the only means of preparing a sample solution for flame photometric analysis.

Dimethylformamide as Solvent for Flame Photometric Analysis and Establishment of Measurement Conditions.—Dimethylformamide (DMF) was chosen as the solvent, which dissolves not only many organic compounds, but also copper compounds to an extent of over 17.5% of cupric nitrate (trihydrate), over 15% of cupric chloride (dihydrate), 1.8% of cupric sulfate, and even a small amount of cupric acetate.

When DMF is used as solvent, the fuel gas pressure, especially the pressure and the flow rate of hydrogen, greatly affect the excitation of the objective cuprous chloride and the interfering C_2- Swan band and cupric oxide spectra. At hydrogen pressure of more than 0.14 kg./cm²(2 lb./in² gauge) the flame becomes very large by inflammation of DMF, attaining a height of over 10 cm., and the emission becomes unstable. The spectral curve obtained in such a case is covered by the C_2-Swan band, cupric oxide and cuprous hydride spectra, and cuprous chloride spectrum are hardly ever distinguishable.

With the decrease of hydrogen pressure, the flame becomes smaller and the effect of interfering spectra lessens gradually, with the appearance of a peak of cuprous chloride band spectrum.

When oxygen pressure is elevated, such as to 1.76 kg./cm²(25 lb./in² gauge), in order to strengthen the spraying of the sample,

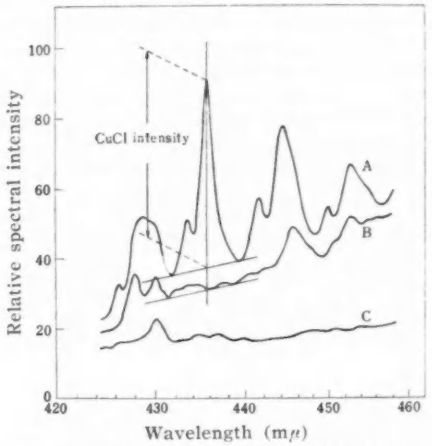

Fig. 2. Spectrum of cuprous chloride.
A (Cu: 0.05 M, Cl: 0.05 M)
B (Cu: 0.05 M)
C (DMF only)
Slit width: 0.05 mm.

6) R. W. B. Pearse and A. G. Gaydon, "Identification of Molecular Spectra", Chapman and Hall, Ltd., London (1950).

and hydrogen pressure is adjusted to about 10 cm. water column, cuprous chloride band spectrum gives a distinguished peak, as indicated in Fig. 2.

The slit width was fixed at 0.05 mm., at which the fine structure of cuprous chloride band spectrum can be observed, and the sensitivity was adjusted accordingly. The relationship between the slit width and the cuprous chloride band spectrum is indicated in Fig. 3.

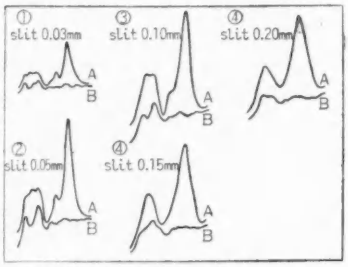

Fig. 3. Effect of slit width on cuprous chloride spectrum.
A (Cu: 0.05 M, Cl: 0.04 M)
B (Cu: 0.05 M)

Preparation of Calibration Curves and Stability of Intensity.—As shown in Fig. 2, a base-line connecting two minima, 431 mμ and 439 mμ, was drawn on a recorded spectral curve, and the height from this line to the top of the peak was taken as the intensity of the cuprous chloride band, whose values were used for preparing the calibration curve.

The concentration of copper affects the stability of the flame and the intensity of the cuprous chloride band and the background. At a low concentration, sufficient intensity can not be obtained; at a high concentration, the background intensity increases and the flame becomes unstable. Examination with various concentrations of copper showed the optimal concentration to be 0.05 M of copper.

An example of calibration curve at 0.05 M of copper is indicated in Fig. 4.

In the range of this calibration curve, the intensity becomes most stable in a chloride concentration of 0.02~0.05 M and is available for determination.

Table II gives the stability of cuprous chloride intensity of 0.02 M and 0.05 M chloride concentration.

TABLE II. REPRODUCIBILITY OF CUPROUS CHLORIDE INTENSITY
(concentration of copper: 0.05 M)

Concentration of chloride	
0.02 M	0.05 M
19.8	45.4
19.8	45.6
20.3	45.2
19.5	45.9
18.9	46.1
19.6	45.4
19.9	45.0
19.0	44.9
$\overline{X}=19.6_0$	$\overline{X}=45.4_4$
$\sigma=\pm0.4_4$	$\sigma=\pm0.4_0$

Effect of Moisture.—Sample solution absorbs moisture when left in an open vessel in high humidity and its intensity

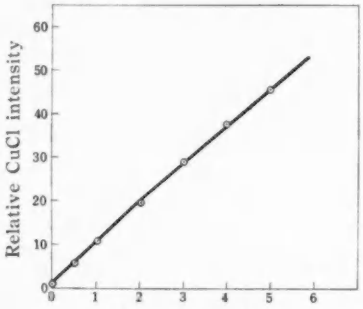

Fig. 4. Calibration curve of chloride.

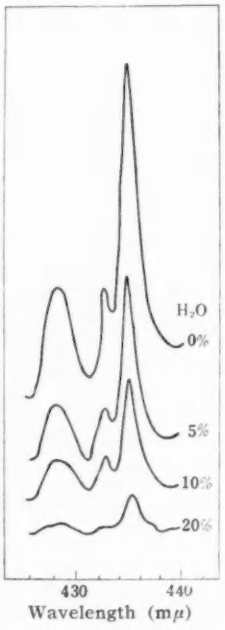

Fig. 5. Effect of moisture on cuprous chloride spectrum.
Cu: 0.05 M, Cl: 0.05 M

TABLE III. DETERMINATION OF VARIOUS ORGANIC CHLORINE COMPOUNDS

Compounds	M.W.	Cl No.	Cl Equivalent	Concn. of Cl (taken)	Concn. of Cl (found)	Recovery %
Chloramphenicol	323.14	2	161.57	0.0257	0.0261	101.5
				0.0398	0.0394	99.0
				0.0514	0.0504	98.1
Monochloroacetic acid	94.50	1	94.50	0.0325	0.0328	100.9
				0.0491	0.0484	98.6
				0.0573	0.0578	100.8
Dichloroacetic acid	128.95	2	64.48	0.0461	0.0469	101.6
				0.0491	0.0501	102.0
Trichloroacetic acid	163.40	3	54.47	0.0237	0.0240	101.3
				0.0418	0.0416	99.6
				0.0474	0.0476	100.5
Chlorobutanol	177.47	3	59.16	0.0227	0.0229	100.9
				0.0454	0.0461	101.6
				0.0428	0.0428	100.0
α-Chloroacetamide	93.52	1	93.52	0.0267	0.0262	98.1
				0.0497	0.0489	98.5
2,4-Dinitrochlorobenzene	202.56	1	202.56	0.0287	0.0290	101.0
				0.0392	0.0380	97.0
				0.0574	0.0582	101.4
Chloramine-T	281.70	1	281.70	0.0237	0.0240	101.3
				0.0338	0.0326	96.5
				0.0474	0.0406	85.6
Procaine hydrochloride	272.77	1	272.77	0.0393	0.0425	108.1
				0.0206	0.0219	106.3
Chloroform	119.39	3	39.80	0.0589	0.0646	109.6
				0.0677	0.0763	112.6
Carbon tetrachloride	153.84	4	38.46	0.0563	0.0725	128.8
				0.0564	0.0717	127.1

will diminish. Hence the determination should be carried out as rapidly as possible after the sample has been transferred to a beaker. The effect of moisture on the spectral curve is shown in Fig. 5.

Determination of Chlorine in Organic Compounds.—Results obtained by the application of the present method to 11 kinds of organic chlorine compounds are shown in Table III.

These results indicate that the amount of chlorine found in solid organic chlorine compounds is approximately 98~102% of the theoretical value, while the value differs greatly from that calculated for liquid organic chlorine compounds, chloramine-T, and procaine hydrochloride. The values are higer by approximately 30% for carbon tetrachloride, and 10% for chloroform, and very arbitrary for chloramine-T.

Such a discrepancy may be due to the change in the intensity of the cuprous chloride band by the characteristic effect of evaporation rate for carbon tetrachloride and chloroform, by the ionic nature of chlorine of procaine hydrochloride, and by the sodium that forms a salt for chloramine-T. However, further detailed examination is still required.

Range of Application.—It is possible to carry out the qualitative and the quantitative determination of chlorine by dissolving organic chlorine compounds in DMF in a chlorine concentration of over 0.005 M and using 2~5 cc. of this solution. It is considered possible that this method can be used as a simple procedure for organic elementary analysis.

Organic compounds containing bromine or iodine can also be determined as in the case of chlorine at approximately the same wavelength region but the band spectra of cuprous bromide or cuprous iodide present less intensity than that of chloride under the same condition.

It is hoped that further research will be made on the determination of compounds containing bromine or iodine.

Summary

Examinations were made on the band spectrum of cuprous chloride based on the Beilstein's reaction in oxy-hydrogen flame. Determination of chlorine in organic chlorine compounds was attempted by using dimethylformamide containing

copper as a solvent and a band peak of 435.4 mμ of cuprous chloride.

In order to decrease the effect of C_2-Swan band that is produced on combustion of organic compounds, and to increase the sensitivity of cuprous chloride band spectrum, combustion gas was maintained at high oxygen pressure; 1.76 kg./cm^2 (25 lb./in^2 gauge), and low hydrogen pressure; 1st, 0.035 kg./cm^2 (0.5 lb./in^2 gauge), 2nd, 10 cm. water column.

γ-BHC was used as the standard and determination was carried out on 11 kinds of organic chlorine compounds, and good results were obtained with samples other than liquid, metal salts, and hydrochlorides. The determinable range for chlorine is 0.005~0.1 M concentration.

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Confirmation of the Formation of Colloidal Particles in Aqueous Cobalt Salt Solution by Radiotracer Electrodialysis

By Tsunetaka SASAKI and Katsuyoshi OSAKA*

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It has been pointed out by a series of our experiments[1] as well as of others[2], that polyvalent metallic ions such as aluminum, iron, copper and thorium exhibit remarkable effects in regard to surface-chemical properties, for instance, wettability of paraffin by water and the nature of monomolecular films of fatty acids. Such effects were explained by the assumption that these ions when dissolved in water mainly exist as hydrated polynuclear ions in a region of suitable pH, rather than as simple monomeric ions, as in the case of alkali and alkaline earth metal ions which show no remarkable effects in regard to the surface-chemical properties. Such an assumption of the existence of aggregated ions has also been proposed by Haissinsky[2] to explain a large fluctuation in the published data on the solubility product of one and the same insoluble compound. McGee, Kraus, Milburn and Kohlschütter[3] also offered similar opinions. Thus the existence of the polynuclear structure becomes increasingly convincing. However, all of these experimental evidences are rather indirect in nature. As a more direct evidence of the existence of such polynulear ions, we can also refer to a number of studies upon radiocolloid formation which proved the existence of colloidal particles in extremely dilute solutions of polonium, bismuth, lead, thorium, yttrium, etc.[4] In more concentrated solutions, the formation of aggregated particles were also observed in cobalt salt solution, for instance, by a self-diffusion method[5].

The present authors have also carried out the experiment of radiotracer electrodialysis[6], coupled with an ordinary filtration, to obtain a direct evidence of the formation of colloidal particles in an aqueous cobalt salt solution.

Experimental

(1) Radiotracer Electrodialysis.—The apparatus employed in the experiment was shown in Fig. 1. In this figure, A is a glass U-tube with one end somewhat wider than the other.

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1) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951); M. Muramatsu and T. Sasaki, ibid., **25**, 21 (1952), **29**, 35(1956); A. Inaba, ibid., **25**, 174(1952); G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.*, **46**, 475 (1950), **47**, 788 (1951).

2) M. Haissinsky, "Les Radiocolloides", Hermann et Cie, Paris (1934); I. Adler and J. Steigman, *J. Phys. Chem.*, **36**, 493 (1952).

3) C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949); K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954); R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955); H. W. Kohlschütter et al., *Z. anorg. allgem. Chem.*, **248**, 319 (1941); H. W. Kohlschütter, *Kolloid-Z.*, **96**, 237 (1941).

4) J. Schubert and E. E. Conn, *Nucleonics*, **4**, No. 6, 2 (1949).

5) R. Matuura and H. Kimizuka, This Bulletin, **28**, 668 (1955).

6) T. Godlewski, *Kolloid-Z.*, **14**, 229 (1914); F. Paneth, ibid., **13**, 297 (1913).

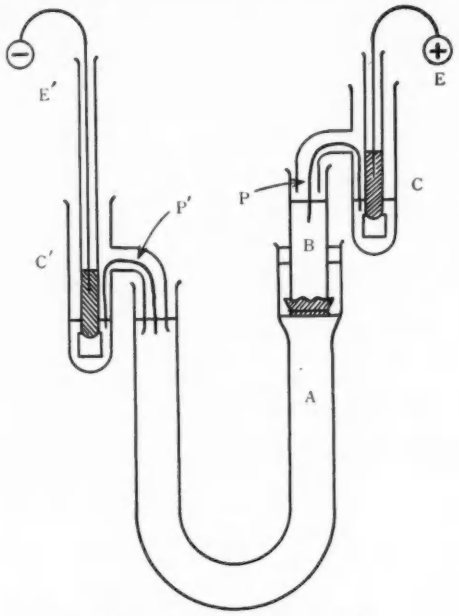

Fig. 1. Electrodialysis cell.

B is a glass cylinder, to the bottom of which a semipermeable cellophane membrane is tightly attached as shown in the figure, with the aid of a rubber ring. The electrode cells C and C' consist of two platinum electrodes E, E' and filter paper bridges P, P'. To carry out an experiment, the tubes A, B and cells C, C' are all filled with the same solution to be studied, that is 10^{-3} mol./l. aqueous solution of cobaltous chloride, with the exception that the solution in B alone is especially tagged with a suitable amount of radioisotope cobalt-60 as a tracer. Hereby, care should be taken that the lower end of the tube B is so placed that it just touches the surface of the solution in A. Now, when we apply D.C. voltage to the electrodes as indicated in Fig. 1, the cobalt ions will move from C to C'. So they will pass through the cellophane membrane downwards, if they are in a state of single ions or relatively small aggregates, while they will not be able to pass through the membrane if they exist as colloidal particles or even larger particles. Thus we can confirm the formation of particles larger than a colloidal size, when we trace the change in concentration of the solution in A.

Now, we have determined a suitable condition for practice from a preliminary experiment. It was evident that the amount dialyzed increased with the increase of applied potential gradient, as well as with the duration of electric current passed, but we performed a 50 volt and 15 minute dialysis*, since prolonged dialysis disturbed the steady condition of the solution to be dialyzed**. After the dialysis, the tube B was removed, 1 cc. of solution in the tube A just below the tube B was taken, heated to dryness in a stainless steel dish, and the radioactivity due to cobalt-60 was measured by a GM counter, as in the usual manner. The permeability was then expressed in c.p.m. Hereby, the GM tube was masked against β-ray and counting was taken only for that due to γ-ray, since the counting due to β-ray fluctuated sensitively for apparently identical geometry of counting arrangement. The cellophane used was a commercial product of a suitable thickness, which was cut in 5×5 cm^2 pieces, and was kept in distilled water for a long time in order to swell the sheets sufficiently for use.

In the course of experiments we found that the permeability of cellophane fluctuated from one sample to another, and also that one and the same sample gradually lost its permeability when used repeatedly. To overcome these undesirable conditions, we used the same membrane only for a couple of measurements, that is, for the permeability measurement of the reference solution containing 10^{-3} mol./l. cobaltous chloride, kept at pH 1, and for the subsequent measurement of the solution to be studied, which was of the same concentration but varying in pH. The control of pH was made using hydrochloric acid and sodium hydroxide.

From the measured permeability, we calculated the relative permeabilty, by the following formula,

$$P_r = \frac{\text{Permeability at pH}=x}{\text{Permeability at pH}=1}$$

The value P_r was used for further discussion. The change of pH due to the electrodialysis was about 0.5 at most.

Before use, cellophane membrane was also examined against pin holes by measuring a leak of Congo red solution through the membrane into pure water for 24 hours, from which we could confirm the fact that the membrane was free from eventual large pores, and also that the

TABLE I. PERMEABILITY OF AQUEOUS COBALT IONS THROUGH CELLOPHANE MEMBRANE

Permeability P_1 at pH=1	Permeability P' at pH=x	P	$P_r=P/P'$
170 cpm	1.0	285 cpm	1.67
173	2.2	92	0.53
146	2.8	52	0.36
163	2.9	97	0.60
188	4.5	104	0.55
169	5.4	119	0.70
136	6.7	50	0.37
148	8.1	44	0.30
144	10.4	0	0

* The distance between the two electrodes is 22 cm.

** The flow of water due to the hydrostatic pressure of water in the tube B was negligible during the period of experiment.

membrane acted as a sieve for particles at least larger than the Congo red molecule. Stock aqueous solution was kept at pH=1 and made up to a desired pH immediately before use. Permeability at varying pH and corresponding P_r values were listed in Table I.

(2) **Filtration.**—Ordinary filtration was carried out to detect the formation of particles coarser than colloidal ones in aqeous solution of cobalt salt. Radioactive cobalt salt solution of the same origin as used in the electrodialysis was filtered under varying pH using fine pore filter paper (Tôyô 5C) and a cobalt content in the filtrate was analyzed by measuring radioactivity due to the aliquot of the filtrate in the same manner as in the preceding experiment. The results were shown in Table II. In this table we showed the amounts of the cobalt ion in solution before and after the filtration by an arbitrary unit of radioactivity of 1 cc. of respective solution which was considered to be proportional to the concentration of cobalt ion. The degree of permeability of cobalt ion was expressed by the ratio F_r of radioactivities in a solution before and after the filtrations as shown in the last column of Table II.

TABLE II. PERMEABILITY OF AQUEOUS COBALT ION THROUGH FILTER PAPER (TÔYÔ 5C)

pH	Amount of cobalt (cpm) before filtr. (A)	after filtr. (B)	$F_r=(B)/(A)$
2.5	287*	288*	1
6.6	882	874	0.99
8.4	883	774	0.88
8.9	873	772	0.88
9.4	874	336	0.38
10.1	846	15	0.017

* Geometry of the counting arrangement was accidentally different from the rest of the measurements.

Discussion

From Tables I and II, we prepared a diagram showing a pH dependence of permeability of cobalt ions through cellophane membrane and filter paper as shown in Fig. 2. In constructing this diagram, we first plotted P_r against pH, excluding the value at pH 1 which showed an extreme deviation, and obtained a curve which as a whole gave a plateau in the region of pH from 2 to 6. Next, we plotted F_r against pH and a similar curve was obtained. Then we adjusted the units of P_r and F_r axes so that both curves coincided at their plateau portions, assuming that there the complete passage of solute took place for both operations.

Now, in Fig. 2, we can readily recognize that the cobalt ions in the region A pass through both cellophane membrane and

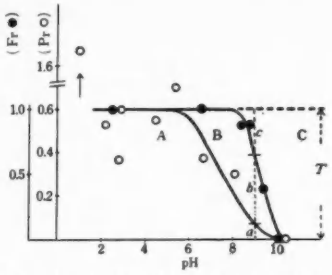

Fig. 2. State of dispersion of aqueous cobalt ion.
A, simple ionic dispersion
B, colloidal dispersion
C, macroscopic aggregation
T, total amount of cobalt in water

filter paper, while those belonging to the region B pass through the filter paper but are retained by the cellophane membrane, and those belonging to the region C are retained both by cellophane membrane and filter paper. Therefore, when we draw an ordinate at a certain pH, a portion a of the ordinate belonging to the region A represents a fraction of an amount of cobalt in the state of A region (simple ionic state), and so on. Thus, in the region of pH from 6 to 10, we confirm the formation of colloidal cobalt particles as those permeable to filter paper but not to cellophane membrane. We can also see the initiation of macroscopic agglomerate formation at pH 8 and precipitation of practically all cobalt ions at pH larger than 10, in the aqueous cobalt salt solution.

Now, from the published data of the solubility product[7], we calculated the minimum pH required to initiate cobaltous hydroxide precipitate in 10^{-3} molar aqueous cobalt salt solution. It was about 6.8, which happened to be situated between pH values of the initiation of colloidal particle formation and macroscopic agglomerate formation. We can conclude from these facts that in the solution studied, there exists a pH region of colloidal particle formation somewhere near the pH, beyond which solubility is exceeded. This conclusion is consistent with the results of a series of our former investigations already mentioned[1].

It must be added that the dissolved state of cobalt ion in aqueous solution changes gradually in the course of time, in a higher pH region as seen from the

7) Landolt-Börnstein, "Physikalisch-chemische Tabellen", I. Erg., Verlag J. Springer, Berlin, (1927), p. 662.

change of color of the solution. So we may expect that the boundary between the A regions and B of Fig. 2 will gradually shift presumably to the left in the course of time. The boundary may also shift according to the nature of the semipermeable membrane used.

Summary

(1) Dissolved state of cobalt ions in 10^{-3} molar aqueous solution of cobaltous chloride, varying in pH, was studied by a radiotracer electrodialysis coupled with an ordinary filtration.

(2) Formation of colloidal particles permeable to filter paper but not permeable to cellophane membrane were confirmed in the solution, in the region of pH from 6 to 10.

(3) Macroscopic precipitates of cobaltous hydroxide began to form at about pH 8 and practically all cobalt ions were precipitated at a pH greater than 10.

(4) The value of pH of insoluble cobaltous hydroxide formation in aqueous 10^{-3} molar cobalt salt solution calculated from the solubility product of cobaltous hydroxide was found to be situated between the pH of the initiation of colloidal particle formation and the pH of the initiation of macroscopic agglomerate formation.

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The Mannich Base of Troponoid and its Application. I. Synthesis of 5-Hydroxymethyl and 5-Formyltropolone Derivatives

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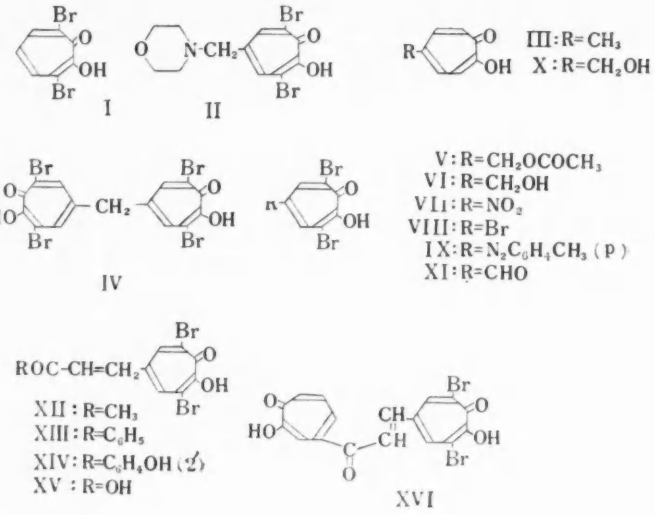
Hartwig[1] reported morpholinomethyl derivatives of tropolone, 3-bromotropolone and 5-bromotropolone, and Pauson[2] also gave a brief description on piperidino methyltropolone in his review. However, Mannich reaction of 3,7-dibromotropolone (I) has not been reported. The present authors applied Mannich reaction to I in order to introduce a carbon chain to the 5-position of the tropolone nucleus and obtained 3,7-dibromo-5-morpholinomethyltropolone (II) in a good yield, from which 5-hydroxymethyl and 5-formyl compounds were derived. This paper describes these results.

When I was treated with morpholine and formalin in acetic acid, II was obtained as yellow powder. II is sparingly soluble in water and usual organic solvents, produces a hydrochloride difficultly soluble in water when treated with hydrochloric acid and gives a green color to the water layer with ferric chloride. Catalytic hydrogenolysis of II in the presence of palladium-carbon gave 5-methyltropolone (III)[3]. This indicates that the morpholinomethyl group of II has taken 5-position in the tropolone nucleus. 3,7-Dibromo-5-acetoxymethyltropolone (V) was obtained when II was heated with a large excess of acetic acid. If a small quantity of acetic acid is used, bis-(3,7-dibromotropololon-5-yl) methane (IV) is formed as a by-product. IV was also formed when II was treated with formalin and dimethylamine in acetic acid or V was heated in aqueous hydrobromic acid. V was easily hydrolyzed by alkali to give 3,7-dibromo-5-hydroxymethyltropolone (VI). The hydroxymethyl group of VI is readily displaced by other groups. For example, 5-nitro (VII)[4], 5-bromo (VIII)[5]

1) E. Hartwig, *Angew. Chem.*, **66**, 605 (1954).
2) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).
3) T. Nozoe, T. Mukai and K. Matsui, *Proc. Japan Acad.*, **27**, 646 (1951).
4) K. Yamane, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 787 (1955); T. Nozoe, Y. Kitahara, K. Doi and T. Arai, *Bull. Chem. Research Inst. of Non-Aqueous Solutions, Tohoku Univ.*, **7**, 13 (1957).
5) T. Nozoe et al., *Proc. Japan Acad.*, **26**, 38 (1950).



and 5-azo (IX)[6] compounds were yielded by the reactions of VI with dinitrogen tetroxide, *N*-bromosuccinimide and diazonium salt respectively.

Sebe and Matsumoto[7] obtained the formyl derivative by oxidizing 3-hydroxymethyltropolone derivatives with activated manganese dioxide. The application of this method to VI gave 3,7-dibromo-5-formyltropolone (XI). Catalytic hydrogenolysis of VI afforded 5-hydroxymethyltropolone (X) which was an unstable substance. Oxidation of X with manganese dioxide gave 5-formyltropolone[8].

3,7-Dibromo-5-formyltropolone (XI) gives an acetal, reacts with various ketonic reagents and produces Schiff's base with aniline. Furthermore, the reactions of XI with acetone, acetophenone, 2-hydroxyacetophenone, malonic acid and 4-acetyltropolone[9] gave 3,7-dibromo-5-(γ-oxobutenyl)tropolone (XII), 3,7-dibromo-5-(γ-phenyl-γ-oxopropenyl)tropolone (XIII), 3,7-dibromo-5-[γ-(2'-hydroxyphenyl)-γ-oxopropenyl]tropolone (XIV), 3,7-dibromo-5-(β-carboxyethenyl)tropolone (XV), and 3,7-dibromo-5-[γ-(tropolone-4'-yl)-γ-oxopropenyl]tropolone (XVI) respectively.

Further experiments of 5-hydroxymethyl and 5-formyltropolone derivatives are in progress.

6) S. Ito, unpublished work.
7) E. Sebe and S. Matsumoto, *Sci. Repts. Tohoku Univ., Ser.* I., **38**, 308 (1954).
8) J. W. Cook et al., *J. Chem. Soc.*, **1952**, 4416.
9) T. Nozoe, K. Takase and M. Ogata, *Chem. and Ind.*, **1957**, 1070.

Experimental[10]

3,7-Dibromo-5-morpholinomethyltropolone (II).—To a stirred mixture of 2 g. of 3,7-dibromotropolone (I), 3 ml. of acetic acid and 2 ml. of morpholine was added 1 ml. of formalin at 70°. The mixture became a clear orange solution and after a few min. a yellow precipitate began to deposit. Thereafter, stirring was continued at 80~90°C for 2 hr. Then 5 ml. of water was added to the cooled reaction mixture. The precipitate, 3,7-dibromo-5-morpholinomethyltropolone (II) was collected and washed with water. Yield, 2.6 g., m. p. 198~200°C.

Anal. Found: C, 38.40; H, 3.55; N, 3.82. Calcd. for $C_{12}H_{13}O_3NBr_2$: C, 38.00; H, 3.43; N, 3.70%. U. V. λ_{max}^{MeOH} (log ε): 268 mμ (4.32), 344 mμ (4.00), 427 mμ (3.92).

Hydrochloride of II; m. p. 225°C (decomp.).

Anal. Found: C, 34.65; H, 3.57; N, 3.35. Calcd. for $C_{12}H_{14}O_3NBr_2Cl$: C, 34.61; H, 3.61; N, 3.36%.

5-Methyltropolone (III).—When 500 mg. of II in aqueous sodium hydroxide was shaken with hydrogen at room temperature in the presence of palladium-carbon, 3 molar equivalents of hydrogen were absorbed. The catalyst was removed by filtration and the filtrate was acidified. A precipitate thereby formed was crystallized from benzene to give 5-methyltropolone (III) as colorless crystals, m. p. 109~110°C, undepressed by admixture with an authentic specimen.

Bis-(3,7-dibromotropolone-5-yl)methane (IV).—To a mixture of 500 mg. of I, 400 mg. of aqueous dimethylamine (40%) and 2 ml. of acetic acid was added 320 mg. of formalin (37%) at 90°C with stirring. After 40 min. the reaction mixture was cooled. Yellow crystals thereby formed

10) Melting points are not corrected.

were collected and washed with a small quantity of methanol. Yield 450 mg., m. p. 225°C (decomp.).

Anal. Found: C, 31.37; H, 1.23. Calcd. for $C_{15}H_8O_4Br_4$: C, 31.48; H, 1.40%. U. V. λ_{max}^{MeOH} (log ε): 272 mμ (4.48), 345 mμ (4.16), 430 mμ (4.07).

When an aqueous solution of ferric chloride was added to a suspension of IV in benzene, a black solid formed at the interface of the benzene and aqueous layers.

Heating of 5-acetoxymethyl compound (V) in aqueous hydrobromic acid under reflux also gave IV.

3,7-Dibromo-5-acetoxymethyltropolone(V).—A suspension of 1 g. of II in 35 ml. of acetic acid was heated at 100°C for 1 hr. and then at 120° for 3 hr. with stirring. The mixture became a yellow solution. When it was cooled, pale yellow needles separated out. The crystals (0.5 g.) were collected. Concentration of the filtrate at 60°C under reduced pressure gave a further crop (0.2 g.). Recrystallization of the combined crystals from ethyl acetate afforded 3,7-dibromo-5-acetoxymethyltropolone (V), m. p. 184~185°C.

Anal. Found: C, 34.66; H, 2.64. Calcd. for $C_{10}H_8O_4Br_2$: C, 34.09; H, 2.27%. U. V. λ_{max}^{MeOH} (log ε): 265 mμ (4.64), 345 mμ (4.14), 425 mμ (4.06).

3,7-Dibromo-5-alkoxymethyltropolone.—Heating of V in methanol under reflux gave 3,7-dibromo-5-methoxymethyltropolone as pale yellow crystals, m. p. 135°C.

Anal. Found: C, 34.08; H, 2.64. Calcd. for $C_9H_8O_3Br_2$: C, 33.33; H, 2.47%.

3,7-Dibromo-5-ethoxymethyltropolone, m. p. 100°C, was similarly obtained.

Anal. Found: C, 35.19; H, 3.33. Calcd. for $C_{10}H_{10}O_3Br_2$: C, 35.54; H, 2.96%.

3,7-Dibromo-5-hydroxymethyltropolone (VI).—A mixture of 1 g. of V, 5 ml. of 3 N sodium hydroxide and 0.5 ml. of ethanol was heated on a water bath for 5 min. with stirring. After being cooled, the reaction mixture was acidified with 6 N hydrochloric acid and a precipitate thereby formed was collected, washed with water and crystallized from methanol to give 3,7-dibromo-5-hydroxymethyltropolone (VI) as pale yellow needles, m. p. 164~165°C. Yield, 0.8 g.

Anal. Found: C, 31.35; H, 1.79. Calcd. for $C_8H_6O_3Br_2$: C, 30.97; H, 1.93%. U. V. λ_{max}^{MeOH} (log ε): 266 mμ (4.47), 345 mμ (4.12), 425 mμ (4.09).

Reaction of VI with Dinitrogen Tetroxide.—To a solution of 0.1 g. of VI in 40 ml. of chloroform was added 0.5 g. of dinitrogen tetroxide with ice-cooling. After being kept for 30 min. at room temperature, the solvent and excess reagent were removed under reduced pressure. Yellow crystals thereby formed failed to show any depression of m. p. on admixture with an authentic 3,7-dibromo-5-nitrotropolone (VII), m.p. 145~146°C.

Reaction of VI with *N*-Bromosuccinimide.—A mixture of 50 mg. of VI, 30 mg. of *N*-bromosuccinimide and 6 ml. of chloroform was boiled for 2 hr. After removal of succinimide by filtration, the filtrate was evaporated to give 50 mg. of colorless crystals, m. p. 124~125°C, undepressed by admixture with 3,5,7-tribromotropolone (VIII).

Reaction of VI with Diazonium Salt.—To a pyridine solution of 50 mg. of VI was added a solution of diazonium salt prepared from 30 mg. of *p*-toluidine. A red precipitate thereby formed was collected, washed with methanol and crystallized from methanol to give red prisms, m. p. 190~191°C, undepressed by admixture with 3,7-dibromo-(*p*-tolylazo)tropolone (IX).

5-Hydroxymethyltropolone (X).—A suspension of 350 mg. of VI in aqueous sodium hydroxide was shaken with hydrogen at room temperature in the presence of palladium carbon. After absorption of 2 molar equivalents of hydrogen and removal of the catalyst by filtration the filtrate was acidified. A small amount of yellowish brown precipitate thereby formed was removed by filtration and the filtrate was extracted with ethyl acetate. Evaporation of the solvent from the extract afforded 5-hydroxymethyltropolone (X) as colorless needles, m. p. 131~132°C. Yield, 100 mg.

Anal. Found: C, 62.82; H, 5.32: Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.27%. U. V. λ_{max}^{MeOH} (log ε): 233 mμ (4.40), 323 mμ (4.01).

5-Formyltropolone.—A mixture of 50 mg. of X, 5 ml. of acetone and 200 mg. of activated manganese dioxide was stirred for 2 days at room temperature. After removal of excessive manganese dioxide by filtration, the filtrate was concentrated to give a yellow manganese salt which was treated with 6 N hydrochloric acid and extracted with ethyl acetate. Evaporation of the extract left 20 mg. of 5-formyltropolone, m. p. 181°C.

3,7-Dibromo-5-formyltropolone (XI).—A mixture of 1 g. of X, 40 ml. of acetone and 4 g. of manganese dioxide was stirred for 20 hr. at room temperature. The mixture was then separated into a solid A and a filtrate B. Removal of the solvent from filtrate B under reduced pressure afforded a yellowish brown manganese salt. Treatment of the salt with 6 N sulfuric acid yielded a yellow precipitate which was crystallized from benzene to give 3,7-dibromo-5-formyltropolone (XI) as yellow prisms, m. p. 175~176°C. Extraction of solid A with acetone by means of a Soxhlet extractor gave a further crop of manganese salt which was also treated similarly to give XI. Yield, 0.95 g.

Anal. Found: C, 31.39; H, 1.43. Calcd. for $C_8H_4O_3Br_2$: C, 31.17; H, 1.30%. U. V. λ_{max}^{MeOH} (log ε): 260 mμ (4.21), 382 mμ (4.31), 410 mμ (4.33).

Heating of XI with methanol gave the acetal as colorless needles, m. p. 135°C.

Anal. Found: C, 33.58; H, 2.79. Calcd. for $C_{10}H_{10}O_4Br_2$: C, 33.90; H, 2.82%. U. V. λ_{max}^{MeOH} (log ε): 265 mμ (4.43), 350 mμ (4.02), 430 mμ (4.21).

Oxime of XI, yellow needles, m. p. 212~213°C.

Anal. Found: N, 4.21. Calcd. for $C_8H_5O_3NBr_2$: N, 4.35%. U. V. λ_{max}^{MeOH} (log ε): 270 mμ (4.42), 372 mμ (4.43), 433 mμ (4.10).

Semicarbazone of XI, yellow granular crystals, m. p. 249~250°C.

Anal. Found: C, 29.24; H, 2.18; N, 10.72. Calcd. for $C_9H_7O_3N_3Br_2$: C, 29.59; H, 1.92; N, 11.51%. U. V. λ_{max}^{MeOH} (log ε): 273 mμ (4.42), 378

mμ (4.55).

Thiosemicarbazone of XI, orange crystals, m.p. 280~288°C (decomp.).

Anal. Found: C, 28.79; H, 2.13. Calcd. for $C_9H_7O_2N_3SBr_2$: C, 28.35; H, 1.84%. U. V. λ_{max}^{MeOH} (log ε): 289 mμ (4.28), 395 mμ (4.47).

Phenylhydrazone of XI, red needles, m. p. 209~210°C.

Anal. Found: N, 6.97. Calcd. for $C_{14}H_{10}O_2N_2Br_2$: N, 7.04%. U. V. λ_{max}^{MeOH} (log ε): 265 mμ (4.42), 410 mμ (4.58).

2,4-Dinitrophenylhydrazone of XI, red needles, m. p. 257~258°C.

Anal. Found: N, 11.78. Calcd. for $C_{14}H_8O_6N_4Br_2$: N, 11.48%. U. V. λ_{max}^{MeOH} (log ε): 260 mμ (4.41), 440 mμ (4.61).

Schiff's Base of XI. — A mixture of 100 mg. of XI, 1 ml. of aniline and 0.5 ml. of acetic acid was heated on a water bath for 10 min. Deep red crystals thereby formed were recrystallized from methanol. Yield 100 mg., m. p. 209~210°.

Anal. Found: C, 43.61; H, 2.55; N, 3.81. Calcd. for $C_{14}H_9O_2NBr_2$: C, 43.98; H, 2.36; N, 3.67%. U. V. λ_{max}^{MeOH} (log ε): 270 mμ (4.37), 390 mμ (4.40).

Condensation of XI with Acetone. — To a solution of 100 mg. of XI in 1 ml. of acetone was added 0.3 ml. of aqueous sodium hydroxide (10%) with stirring at room temperature. After 2 days, an orange precipitate was collected and acidified with 6 N hydrochloric acid to give a yellow precipitate. Its recrystallization from acetone afforded 100 mg. of 3,7-dibromo-5-(γ-oxobutenyl)tropolone (XII), m. p. 195°C.

Anal. Found: C, 38.19; H, 2.61. Calcd. for $C_{11}H_8O_3Br_2$: C, 37.93; H, 2.30%. U. V. λ_{max}^{MeOH} (log ε): 280 mμ (4.38), 405 mμ (4.56).

Condensation of XI with Acetophenone.— A mixture of 100 mg. of XI, 0.3 ml. of acetophenone and 0.3 ml. of aqueous sodium hydroxide (10%) was stirred for 2 hr. at room temperature. A deep red precipitate thereby formed was collected and acidified with 6 N hydrochloric acid to give a yellow precipitate. Its crystallization from methanol yielded 120 mg. of 3,7-dibromo-5-(γ-phenyl-γ-oxopropenyl)tropolone (XIII), m. p. 200 °C.

Anal. Found: C, 46.16; H, 2.40. Calcd. for $C_{16}H_{10}O_3Br_2$: C, 46.83; H, 2.44%. U. V. λ_{max}^{MeOH} (log ε): 260 mμ (4.14), 288 mμ (4.16), 418 mμ (4.38).

Condensation of XI with 2-Hydroxyacetophenone. — A mixture of 100 mg. of XI, 80 mg. of 2-hydroxyacetophenone, 1 ml. of ethanol, and 0.5 ml. of 6 N sodium hydroxide was stirred on a water bath for 30 min. The mixture became dark red and formed a small quantity of precipitate C. Precipitate C was removed by filtration. Acidification of the filtrate with 6 N hydrochloric acid gave a brown solid. Recrystallization of the solid from methanol afforded 50 mg. of 3, 7-dibromo-5-[γ-(2'-hydroxyphenyl)-γ-oxopropenyl]tropolone (XIV), m. p. 215°C (decomp.).

Anal. Found: C, 45.02; H, 2.60. Calcd. for $C_{16}H_{10}O_4Br_2$: C, 45.11; H, 2.35%. U. V. λ_{max}^{MeOH} (log ε): 260 mμ (4.20), 295 mμ (4.20), 440 mμ (4.54).

Acidification of precipitate C gave XI recovered.

Reaction of XI with Malonic Acid.—A mixture of 100 mg. of XI, 100 mg. of malonic acid, 1 ml. of pyridine and 3 drops of piperidine was heated for 1 hr. at 90°C, for 2 hr. at 100°C and finally for 2 hr. at 120°C. During this time, evolution of carbon dioxide was observed and the mixture turned brown in color. Then the mixture was poured into a mixture of 0.5 g. of ice and 1 ml. of concentrated hydrochloric acid. A brown precipitate thereby formed was crystallized from methanol after decolorization with carbon to give 50 mg. of 3,7-dibromo-5-(β-carboxyethenyl)tropolone (XV), m. p. 195°C.

Anal. Found: C, 34.92; H, 2.01. Calcd. for $C_{10}H_6O_4Br_2$: C, 34.29; H, 1.71%. U. V. λ_{max}^{MeOH} (log ε): 268 mμ (4.39), 380 mμ (4.40).

Condensation of XI with 4-Acetyltropolone.—A mixture of 50 mg. of XI, 40 mg. of 4-acetyltropolone, 0.5 ml. of methanol and 0.5 ml. of aqueous sodium hydroxide (10%) was stirred for 30 min. at room temperature. The mixture turned red in color and deposited a deep red precipitate. The precipitate was collected, acidified with 6 N hydrochloric acid and recrystallized from methanol to give 50 mg. of 3,7-dibromo-5-[γ-(tropolone-4'-yl)-γ-oxopropenyl]tropolone (XVI), m. p. 220°C (decomp.).

Anal. Found: C, 42.93; H, 2.23. Calcd. for $C_{17}H_{10}O_5Br_2 \cdot H_2O$: C, 43.01; H, 2.54%. U. V. λ_{max}^{MeOH} (log ε): 255 mμ (4.24), 430 mμ (4.25).

Summary

Application of the Mannich reaction to 3,7-dibromotropolone gave 3,7-dibromo-5-morpholinomethyltropolone, from which 5-hydroxymethyl and 5-formyl derivatives were derived. It was found that the hydroxymethyl group of 3,7-dibromo-5-hydroxymethyltropolone can be easily displaced, and that 3,7-dibromo-5-formyltropolone has the characteristics of an ordinary aldehyde and reacts with ketones and malonic acid.

For the purpose of this work, 4-acetyltropolone was graciously furnished by Mr. K. Takase (Professor Nozoe's Laboratory, Faculty of Science, Tohoku University). A part of the expenses for the present research was defrayed by Sankyo Co., Ltd. The microanalyses were carried out by Messrs. S. Oyama and S. Azumi and Miss A. Iwanaga. The authors wish to express their sincere gratitude to the above mentioned people.

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Cesium-137 in the Coastal Waters of Japan

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The levels of radioactive cesium-137 in various materials have been analyzed by the authors and their colleagues since May 1957. A part of the results was compiled by Hiyama and presented to the Scientific Committee on the Effects of Atomic Radiation[1]; the full report is to be published in near future. The analytical data from other countries for cesium-137 in various materials are also available in the U.N. Report[2]. However, we have received no information on the level of cesium-137 in sea-water although that of strontium-90 was presented by Bowen in 1957[3]. It is necessary to know the level of the concentration of cesium-137 in oceanic water caused by nuclear fission explosions and also to guess a tolerable discharge rate of radioactive waste, especially for the Japanese people for whom marine products are the principal sources of proteins.

The cumulative ground deposit in Japan of strontium-90 has been shown by Miyake to be about 8 mc/km^2 in June 1957[4], and perhaps this value is also valid for cesium-137, of which the fission yield and the half-life are almost the same. If we consider temporarily that the sea-water is uniformly mixed to the depth of 100 m., then about 80 $\mu\mu$c of cesium-137 is expected to be present in one kilo-liter of sea-water. The sensitivity for cesium-137 measurement was about 100 $\mu\mu$c, and so it was a matter of actual difficulty to deal with kilo-liters of sea-water in the laboratory. Fortunately, domestic salt is commonly produced directly from sea-water in Japan; hence bittern or carnallite of industrial origin could be chosen as the starting material.

The Behavior of Cesium during the Evaporation of Sea-water. — It is a well known fact that cesium and rubidium are enriched in carnallite as compared in sea-water. Jander and Busch found 0.0002% of cesium chloride in Stassfurt carnallite on the average[5]. In the manufacturing process by solar and vacuum evaporation, cesium and rubidium have also been expected to be enriched in bittern and carnallite. The authors performed several experiments by the use of radioactive tracers ^{86}Rb and ^{137}Cs. Small fractions of sodium chloride and potassium chloride were crystallized respectively from their saturated aqueous solution by the isothermal evaporation. Both the activities of the crystal and of the evaporation residue of the initial solution were measured and the logarithmic distribution coefficient λ was calculated from the equation:

$$\lambda \log \frac{\text{NaCl (Total)}}{\text{NaCl(Total)-NaCl(Crystal)}} = \frac{^{137}\text{Cs (Total)}}{^{137}\text{Cs(Total)}-^{137}\text{Cs(Crystal)}}$$

In case of carnallite crystallization, activities were measured for both the initial solution and the mother liquor. The

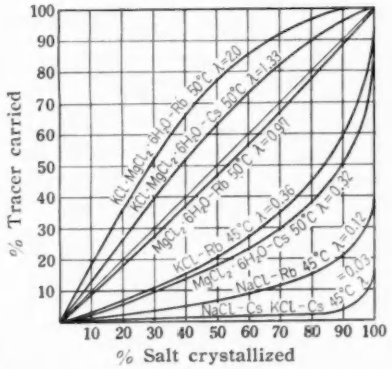

Fig. 1. Efficiency with which the traces of cesium and rubidium are carried by crystallization of several oceanic salts.

1) "Radiological Data in Japan II", edited by Y. Hiyama, Government of Japan, Sept. 1957; U. N. General Assembly A/AC. 82/G/R. 30 (1958).

2) "The Effects of Atomic Radiation", U. N. Report Annex D, A/AC. 82/R. 65/Add. 3 (1958).

3) V. T. Bowen, "Some Geochemical Studies at the Air-Water Interface", presented to the N. R. C. Meteorology Panel, Sept. 25, 1957.

4) Y. Miyake and K. Saruhashi, *Papers in Meteorology and Geophysics*, 8, 242 (1957); U. N. General Assembly, A/AC. 82/R.R. 65/Add. 3 Table XIV (1958).

5) G. Jander and F. Busch, *Z. anorg. u. allg. Chem.*, 187, 165 (1930).

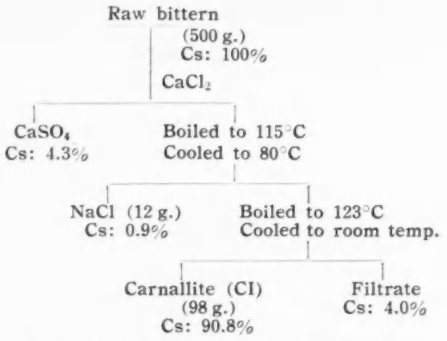

Fig. 2. Loss of cesium in the process of crystallization of carnallite from bittern.

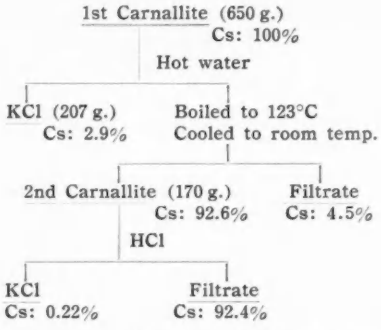

Fig. 3. Loss of cesium in the process of recrystallization of carnallite.

results summarized in Fig. 1[6] are in accord with the fact that cesium and rubidium have been naturally enriched in carnallite, and this nature will be useful for the practical concentration aimed at cesium-137 determination in sea-water. However, as the industrial conditions of carnallite formation greatly differ from the natural, the authors attempted to check the concentration procedure for cesium with a tracer experiment. The procedure and the loss of cesium is schematically shown in Fig. 2; the recovery of cesium is satisfactory.

Recrystallization of Carnallite.—Further enrichment of cesium can be accomplished by fractional recrystallization of carnallite. Halperin and Sambursky applied this method to the determination of rubidium in Dead-Sea carnallites[7]. As easily conceivable from the well-known phase diagram of the system KCl-$MgCl_2$-H_2O, on evaporation of the solution of artificial carnallite which contains a few per cent of sodium chloride, first only sodium and potassium chloride are deposited until the so-called "carnallite point" is reached, where the deposition of carnallite begins. The authors have modified this method for the practical convenience as described below.

A quantity of hot water less than that sufficient for complete dissolving is added to the primary carnallite (CI) and the suspension is cooled with vigorous agitation. Undissolved sodium and potassium chloride are filtered off and the filtrate is boiled until the boiling point reaches 123°C and then cooled to room temperature. The second carnallite (CII) thus obtained is only about one fourth the weight of the primary carnallite and contained 92.6% of the original cesium, so that a fourfold enrichment in concentration of this element can be obtained (Fig. 3).

Another recrystallization of CII resulted in the formation of the third carnallite (CIII) weighing about 600~800 g. which was expected to contain 70~80% of the total cesium originally existing in 50 kg. of bittern. When started from 2.5 kg. of the industrial carnallite sample, only one recrystallization was required to make the mass suitable for the further treatment of cesium separation. The chemical composition of several samples of bittern and carnallite is shown in Table I. An early experiment revealed that only 20 kg. of bittern or 1 kg. of carnallite was sufficient for cesium-137 determination and the later determination were made on this scale.

Separation and Determination of Cesium in Carnallite.—An aliquot of the saturated solution of the final carnallite was reserved for the flame photometric determination of natural cesium and the remainder was made 2.5 N acid with hydrochloric acid after the addition of carrier cesium chloride (100 mg. as Cs). Precipitated potassium chloride was filtered off and to the filtrate was added sodium silicomolybdate solution*) at 60~70°C with constant agitation. After cooling, the precipitate of cesium silicomolybdate was filtered off and washed with 2.5 N hydrochloric acid and then with water. The precipitate was dissolved with the least possible amount of hot 10% solution of sodium hydroxide. The undissolved silica was filtered off and

6) S. Matsuda, *J. Mineral. Soc. Japan* (*Kōbutsugaku-Zasshi*), **3**, 523 (1958).
7) A. Halperin and S. Sambursky, *Bull. Research Council of Israel*, **2**, 107 (1952).

* Prepared by the method of Jander and Busch, loc. cited.

TABLE I. CHEMICAL COMPOSITION OF BITTERN AND CARNALLITE

(g./100 g.)

Location	Sample	KCl	NaCl	$MgCl_2$	$MgSO_4$	Total
Onahama	Bittern	3.84	4.03	19.1	6.43	33.4
	CII	18.6	10.7	31.2	0.24	60.7
	CIII	20.7	8.60	33.0	0.19	62.5
Horobetsu	Bittern	3.28	7.92	16.1	3.56	30.9
	CII	19.0	8.67	31.3	0.45	59.4
	CIII	23.5	5.68	31.2	0.19	60.6
Akao	Carnallite	19.1	14.8	32.7	0.45	67.1
	CII	19.4	7.48	31.7	0.39	59.0
Hōfu	Carnallite	23.9	15.5	31.4	0.67	71.5
	CII	20.6	6.87	31.5	0.16	59.1
Tōji	Carnallite	16.4	5.95	30.9	4.95	58.2
	CII	20.5	5.07	32.2	0.42	58.2
Theor. Carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$		26.8	0	34.3	0	61.1

TABLE II. CESIUM-137 CONCENTRATION IN BITTERN AND CARNALLITE

Loc. No.	Location	Sample No.*	Date of Manufacture	^{137}Cs Conc.	$\mu\mu c$**
1	Horobetsu, Hokkaidō	B-1	Oct. 1957	500	± 21
		B-14	Mar. 1958	200	24
2	Watanoha, Miyagi Pref.	B-13	Mar. 1958	1800	46
3	Onahama, Fukushima Pref.	B-2	Aug. 1957	430	17
		B-3	June 1957	290	33
		B-4	Mar. 1958	270	33
4	Asahi, Chiba Pref.	B-8	Mar. 1958	4950	50
5	Kurobe, Toyama Pref.	B-15	Apr. 1958	220	48
6	Kira, Aichi Pref.	B-12	Mar. 1958	2600	60
7	Akao, Hyōgo Pref.	C-3	Oct. 1957	680	20
		C-6	Mar. 1958	450	15
		B-6	Mar. 1958	1300	40
8	Tōji, Okayama Pref.	C-2	Sept. 1957	1450	58
		C-5	Mar. 1958	1650	46
		B-5	Mar. 1958	1500	52
9	Matsunaga, Hiroshima Pref.	B-7	Mar. 1958	1700	48
		C-4	Mar. 1958	1400	31
10	Hōfu, Yamaguchi Pref.	C-1	June 1956	800	40
11	Naruto, Tokushima Pref.	B-10	Mar. 1958	2100	44
12	Takuma, Kagawa Pref.	C-7	Aug. 1957	1800	46
		C-8	Mar. 1958	1200	83
		B-9	Mar. 1958	1500	55
13	Takada, Ōita Pref.	B-11	Mar. 1958	2500	45

* B indicates bittern and C indicates carnallite sample.

** Computed for the basis of 50 kg. bittern.

after the filtrate was made up to about 300 ml. with water, 10% aqueous solution of chloroplatinic acid was added to precipitate the cesium. The precipitate was washed with water and then with ethyl alcohol, dried at 110°C, weighed and mounted for counting.

Radioassay was performed by β-counting by the use of a shielded GM-tube of the mica end-window type and the result was corrected for the absorption and the scattering of cesium chloroplatinate and the chemical yield. Details of the later steps of separation and radiochemical

determination have already been described[8,9]. Contamination of the final precipitate of cesium chloroplatinate with other fission activities, potassium-40, and rubidium-87 is negligibly small[9].

In the determination of natural cesium, it is necessary to take care, not to introduce contamination resulting from the reagents to be used. As there is no evidence of the absence of a trace of cesium in sodium salt, the dipicrylamine has been chosen as the precipitant for potassium. The reagent can easily be purified and a tracer experiment has proved that potassium dipicrylaminate effectively carries down traces of cesium.

An aliquot of the saturated solution of the final carnallite containing approximately 0.1 g. of potassium was diluted to about 50 ml. and treated with magnesium dipicrylaminate solution. The separation of potassium and cesium from the precipitated dipicrylaminate was accomplished in the simple way by the methyl isobutyl ketone extraction, of which the principle was previously reported[10]. The intensity of cesium 852.1 mμ line was measured in the usual way.

Materials and Results

Fifteen samples of bittern and eight samples of carnallite manufactured during June 1956 and April 1958 were collected around Japan. The location and the date of manufacture are shown in Table II and Fig. 4. The outline of manufacture of salt in Japan must be described to serve for the later discussion. The modern system of manufacture is entirely artificial, driven by electric power. Sea-water is pumped up directly into a vacuum evaporator and is never exposed to the open air, so the consideration about atmospheric contamination during the whole production process is unnecessary. The samples of bittern manufactured by this system are B-1, 2, 3, 4, 14 and 15 in Table II. On the other hand, the other samples have been manufactured by the usual salt-field system. In this case, sea-water is exposed to the open air, so that, we must consider the influence of fall-out during production.

The results are shown in Table II. Four

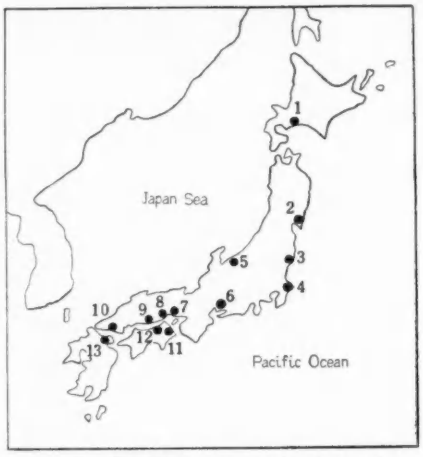

Fig. 4. Locations materials obtained.

kilo-liters of sea-water will produce about 50 kg. of bittern which are equivalent to about 2.7 kg. of carnallite. Values in Table II have been computed on the basis of 50 kg. of bittern. The analytical data for the natural cesium content of several samples are shown in Table III in which the isotopic ratios of cesium-137 and -133 have also been calculated.

The Natural Cesium Content of Sea-water.—Several authors have given surprisingly different values for the cesium content of sea-water. The maximum value is 4.3 μg. whereas the minimum is only 0.002 μg. per liter. The earliest estimate was given by Goldschmidt et al. as 2 μg.[11], although it was not based on actual determination in sea-water. Harada reported values from 0.002 to 0.01 μg.[12] Minami et al. started from about 50 ml. of

TABLE III. ISOTOPIC RATIO OF CESIUM-137 TO -133 IN BITTERN AND CARNALLITE

Sample No.	^{133}Cs mg.	^{137}Cs μμc	^{137}Cs/^{133}Cs $\times 10^9$
B-3	0.21	130	7.7
B-5	0.33	590	22
B-7	0.52	650	16
B-10	0.30	960	40
B-11	0.56	1060	24
B-14	0.26	85	4.1
C-4	0.25	1200	60
C-5	0.22	610	35
C-7	0.33	670	25

8) N. Yamagata et al., *Japan Analyst* (*Bunseki Kagaku*), **7**, 433 (1958).
9) N. Yamagata and T. Yamagata, This Bulletin, **31**, 1063 (1958).
10) N. Yamagata and S. Watanabe, ibid. **30**, 580 (1957).
11) V. M. Goldschmidt et al., *Nachr. Ges. Wiss. Göttingen, Math.-Physik. Klasse*, **1933**, 235.
12) Y. Harada, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaisi*), **64**, 1049 (1943); Those values were apparently misabstracted as 2~10 μg./l. in the *Chem. Abstr.*, **41**, 3394 (1947).

sea-water, by use of the cathode layer emission spectroscopy and gave the value of 0.1~1 μg. per liter[13]. Ishibashi and Hara reported values from 3.4 to 4.3 μg.[14] Recently, the most sensitive radioactivation analysis was applied by Smales and Salmon and the value of 0.5 μg. (±10%) per liter was reported[15]. The relative proportions of the major constituents in sea-water are practically constant, although some of the micro-elements of biological activities may fluctuate with time and space. On account of the strongly ionic nature of this element and its biological insignificancy, we can not guess any proper reason for real fluctuations of the concentration of cesium in the open oceans. In fact, the levels of cesium given by Smales and Salmon have been fixed within narrow limits for sea-water from the Atlantic Ocean including a sample of coastal water. The circumstance is considered also valid for the Pacific Ocean and the coastal waters of Japan. On the assumption that the value of 0.5 μg. is correct for the sea waters around Japan, we should like to proceed with the discussions in the following section.

Discussion

The concentration of cesium-137 in samples other than Location No. 1, 3 and 5 is considerably higher by factors of 5 to 10 or more than that in the latter locations; the trend is clear also in the isotopic ratio. The difference may be attributed principally to the contamination by fall-out during production. We can guess the possible contamination as follows. One of the salt-field systems of obtaining the brine from sea-water is the oldest, called the "Irihama" system and the evaporation is effected principally by the sun. For instance, in March 1958 ,at Watanoha, Miyagi Prefecture (Loc. No. 2), 12 kl. of brine of specific gravity (d_4^{15}=1.125) 16.0° Bé was produced per hectare in two days. Another plan to obtain the brine is a combination of the system of evaporation by the sun and air called the " flowing-down " system. For instance, 120 kl. of sea water is treated per day per hectare by this system. From these figures we can guess the possible contamination of 50 kg. of bittern approximately as 0.3~6 mμc when the fall-out rate of cesium is temporarily assumed to be 0.03~0.3 mc/km^2/month in early 1958.

The above computation indicates that the bittern and the carnallite obtained at the locations other than No. 1, 3 and 5 where salt is produced by the salt-field system are possibly contaminated by fall-out during production to a great extent. Only the results obtained for the bitterns from the locations No. 1, 3 and 5 are reliable to enable us to guess the levels of concentration of cesium-137 in sea-water. On the basis of the approximate figure of the weight of bittern equivalent to the volume of sea water, viz., 50 kg. to 4kl. and of 70% of the over-all yield of cesium, we can compute the concentration of cesium-137 in sea-water approximately to be 70~150 $\mu\mu$c/kl. The values of 160 and 310 $\mu\mu$c/kl. are also derived on the basis that the isotopic ratio of cesium-137 to -133 is 4.1 and 7.7×10^{-9} (Table III) and the cesium-133 content of sea-water is 0.5 μg./l.

The greater part of the domestic salt consumed in Japan comes from sea-salt and an average person takes approximately 15 g. of sodium chloride every day. The average daily intake of cesium-137 by a Japanese in the period from Aug. 1957 to Aug. 1958 is determined by the authors to be 22~56 $\mu\mu$c. The contribution of sea-salt to the total intake of cesium-137 by a person may be roughly computed if the assumption is admitted that the cesium in sea-water moves into the salt during manufacture following the distribution law by the coefficient of 0.03 (Fig. 1). Thus, the weight ratio of Cs/Na in the salt shall be 1.5×10^{-9} as compared with the ratio of 5×10^{-8} in sea-water (calculated from the values, 0.5 μg. of cesium and 10 g. of sodium in one liter). When we take the ratio of cesium-137 to -133 in sea water approximately to be 10^{-8} or 1 mμc of cesium-137 per 1 mg. of cesium-133, 15 g. of sodium chloride shall contain 0.01 $\mu\mu$c of cesium-137. It means that the contribution of sea-salt to the total intake of radioactive cesium-137 by a person is only 10^{-3} or less.

The β-counting equipment used by the authors was a usual mica end-window type GM-counter shielded by lead blocks. Natural background was 10~12 c.p.m. and counting efficiency was 5.3% for cesium-137 by our experimental conditions. About 100 $\mu\mu$c was the minimum amount of cesium-137 to be measured with a standard error of ±10%. Our present program includes the arrangement of a low-level β-counting equipment. With this, only 50~100 liters of sea-water

13) E. Minami, N. Yamagata et al., Read at the Symposium. held by the Chemical Society of Japan for Geochemistry at Nagoya Univ. (1947). Not published.
14) M. Ishibashi and T. Hara, *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 248 (1954).
15) A. A. Smales and L. Salmon, *Analyst*, **80**, 37 (1955).

are sufficient for cesium-137 determination. With a slight modification of the separation method direct separation from sea-water will be possible.

The authors thank those who co-operated or assisted in the collection of bittern and carnallite samples, especially Dr. Jirō Sugi and Dr. Kazuo Shimizu at the Central Research Institute, Japan Monopoly Corporation. The authors also thank Mrs. T. Yamagata and Mr. E. Tajima for advice and assistance in the laboratory. Finacially, this work was partly supported by the Ministry of Education.

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Action of Reducing Agents on Copper Phthalocyanine and its Chlorinated Derivatives

By Masahiro SHIGEMITSU

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Although copper phthalocyanine is a very stable organic pigment, it is decomposed by oxidizing agents in its dissolved state in strongly acid solvents. However, it has been considered so far that copper phthalocyanine is stable toward reducing agents. The author examined the action of reducing agents on copper phthalocyanines containing chlorine in the range of naught to sixteen atoms per molecule and found that they were easily attacked by reducing agents, while copper phthalocyanine containing no chlorine was not. When copper phthalocyanine is chlorinated into "copper phthalocyanine green", its color is darkened from bright green to dark green. The cleavage of phthalocyanine nucleus was not caused by reducing agents, although it was caused by oxidizing agents.

Experimental

Materials.—Syntheses of copper phthalocyanine and chlorinated copper phthalocyanines were carried out as follows.

Copper phthalocyanine.—A mixture of phthalic anhydride, urea and cuprous chloride was heated at about 190°C for 3 hr.[1] The reaction product was treated with 5% hydrochloric acid and 2% sodium hydroxide The precipitate was filtered off, washed with water and ethanol, and dried.

Chlorinated copper phthalocyanines.—One part of copper phthalocyanine was dissolved in 6 parts of a eutectic mixture of aluminum chloride and sodium chloride (9:2, by weight, m. p. 145°C) at 150~160°C, and chlorine gas was introduced at a given flow rate and samples were taken out at regular intervals. These samples were washed with 5% hydrochloric acid, 2% sodium hydroxide, water and ethanol, and nine kinds of chlorinated copper phthalocyanine with chlorine content ranging from 2.91% to 44.97% as the degrees of chlorination were prepared. Copper hexadecachlorophthalocyanine (sample XI in Table I) was prepared by chlorinating copper octa-(3,6)-chlorophthalocyanine[2].

The results of chlorine analysis (micro-Carius method) for eleven samples thus prepared are given in Table I.

Methods.—*Particle size reduction.*—The particle size of these samples prepared as above were too large to be used as pigments. Therefore, the particle size of these samples was reduced

TABLE I. CHLORINE CONTENTS OF THE SAMPLES

Sample	Cl	
	%	atom/mol.
I	0.11	0
II	2.91	0.5
III	15.15	1.8
IV	24.05	5.1
V	25.44	5.5
VI	33.71	8.2
VII	39.57	10.6
VIII	42.86	12.1
IX	43.63	12.5
X	44.97	13.2
XI	50.32	16.0

1) M. Shigemitsu, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 110 (1959) (presented at the 10th Annual Meeting of Chemical Society of Japan held in April, 1957).

2) M. Shigemitsu, ibid., **62**, 110 (1959) (presented at the Autumnal Joint Meeting of Chemical Societies of Japan, Tokyo, 1957).

by the acid pasting method[3]. One part of the sample (I~V) was dissolved in 5 parts of 98% sulfuric acid, while 1 part of the sample (VI~XI) was dissolved in 3 parts of chlorosulfonic acid. Each solution was poured into 70 parts of ice water with stirring. Fine crystals precipitated were filtered off, washed free from acid with water and dried at about 60°C.

*Treatment by reducing agent, rongalit**. — A mixture of 1 g. of the sample treated as in the above section and 30 cc. of 20% aqueous solution of rongalit was heated at 150~155°C for 20 min. in a stainless steel autoclave equipped with a stirrer. The product obtaind was filtered off, washed with water and dried at about 60°C.

Measurement of the spectral reflectance curves. —One part of the sample treated as in the above section and 1.5 parts of polymerized linseed oil were mixed, made into paste by grinding 400 rounds in a Hoover automatic muller. To one part of this paste were added 70 parts of zinc white paste obtained by grinding 2 parts of zinc oxide with 1.5 parts of polymerized linseed oil. Then the mixed paste was applied 0.5 mm. thick on a coated paper with a "bladeoapplicator" (Gardner Laboratory), and the specimen was dried at room temperature. The spectral reflectance of the specimen prepared thus was measured with a General Electric recording spectrophotometer.

Electron microscopic observation of particle forms and measurement of particle size distributions.—To the samples (VI, VII, VIII, IX and X treated as in the above section was added 0.1% aqueous solution of a non-ionic surface active agent and the pigment was thoroughly dispersed with agitation. A drop of the dispersed solution was placed on a collodion film and dried. The electron microphotographs were taken at 2,000 magnification with an electron microscope of Hitachi Works, and the 20,000 magnification was obtained by enlarging photographs ten times. Three hundreds particles photographed were taken out at random, and particle size distributions were calculated by measuring their shorter and longer diameters.

Results

Variation in Chlorine Content.—Chlorine contents of the samples heated in the aqueous solution of rongalit are given in Table II.

As is clear from Table II, samples I to V do not vary in their chlorine content. But samples VI to X, which have greater chlorine contents, show some decrease in chlorine content by the treatment in rongalit. The greater the chlorine content of the sample, the greater the decrease in the chlorine content by the treatment. However, copper hexadecachlorophthalocyanine (XI) shows somewhat smaller decrease in chlorine content.

TABLE II. VARIATION IN CHLORINE CONTENT

Sample	Cl %	
	Original sample	Sample treated by rongalit
I	0.11	0.12
II	2.91	2.86
III	15.15	15.09
IV	24.05	24.12
V	25.44	25.38
VI	33.71	33.32
VII	39.57	39.15
VIII	42.86	42.41
IX	43.63	43.10
X	44.97	44.30
XI	50.32	49.76

Variation in Color.—The luminosity Y, purity P_e and dominant wavelength λ_D calculated after the C. I. E. coordinate system from the spectral reflectance data are given in Table III.

TABLE III. LUMINOSITY, PURITY AND DOMINANT WAVELENGTH OF THE PIGMENTS

Sample		Y %	P_e %	λ_D mμ
I	original	24.80	48.7	479.0
	treated	22.78	40.3	478.8
II	original	19.07	54.2	478.5
	treated	24.13	48.0	479.4
III	original	18.45	56.0	478.2
	treated	21.62	53.7	478.9
IV	original	19.75	58.3	481.0
	treated	21.87	56.0	481.2
V	original	21.77	54.0	482.2
	treated	23.08	52.0	482.0
VI	original	25.13	49.5	484.8
	treated	23.90	47.3	483.3
VII	original	25.63	46.0	486.9
	treated	21.75	45.5	485.2
VIII	original	26.83	40.3	489.8
	treated	20.48	37.0	486.8
IX	original	26.80	41.0	490.8
	treated	20.07	38.5	487.4
X	original	30.33	37.0	491.4
	treated	20.15	39.0	487.5
XI	original	30.34	36.8	492.6
	treated	22.18	39.1	488.9

It is evident from Table III that the variation of color becomes greater with the increase in the chlorine content and diminishes again in copper hexadecachlorophthalocyanine (XI). The relationship between the luminosity change (ΔY%)

3) H. A. Lubs, "Chemistry of Synthetic Dyes and Pigments", Reinhold Publishing Corp., New York (1955), p. 587.

* addition compound of formalin and sodium hydrosulfite.

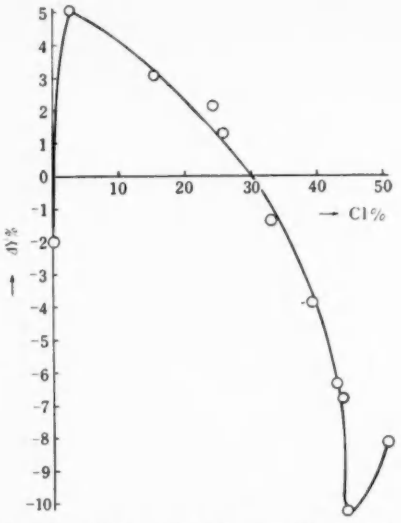

Fig. 1. Relationship between luminosity change and chlorine content.

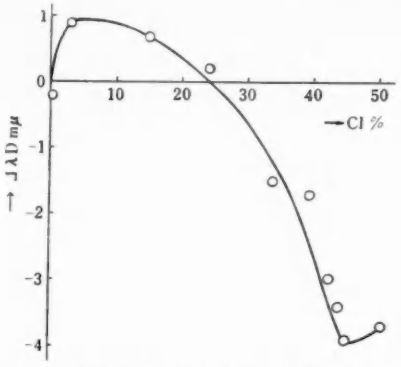

Fig. 2. Relationship between the shift of dominant wavelength and chlorine content.

or shift of dominant wavelength ($\Delta\lambda_D$ mμ) and the chlorine content are shown in Figs. 1 and 2.

It is to be noted that the sample with a greater chlorine content shows a lower brightness in color and shorter dominant wavelength.

Particle Size Distribution of Samples Subject to Remarkable Discoloration.—It is inferred from the above results that darkening of the color of samples treated with reducing agents is accompanied with the change in chemical composition of pigments. However, as the color of pigments, unlike dyes, is largely influenced by the form and the size of particles. particle size distribution of samples subject to remarkable discoloration (VI, VII, VIII, IX and X) was measured. The results are given in Table IV in which d_{mp} denotes the most probable value and d_m the average particle diameter. The value of d_m was calculated from

TABLE IV. PARTICLE SIZE DISTRIBUTION

Sample	Diameter mμ	d_{mp} mμ	d_m mμ	$\pm\delta$ mμ	Form
VI original	110~340	207	235	50	leaflet
	225~450	325	337	49	
VI treated	118~329	213	220	44	〃
	225~452	318	360	59	
VII original	103~370	208	219	52	〃
	230~480	342	343	44	
VII treated	110~370	220	223	48	〃
	240~485	350	354	59	
VIII original	115~320	200	202	45	〃
	220~479	320	337	55	
VIII treated	112~302	210	201	39	〃
	210~480	335	328	47	
IX original	120~322	208	207	42	〃
	240~460	345	339	50	
IX treated	114~330	212	222	44	〃
	250~472	340	347	52	
X original	121~300	204	216	42	〃
	220~450	330	313	54	
X treated	110~302	208	217	38	〃
	243~448	315	331	39	

$$d_m = 1/100 \sum_i f_i d_i$$ [4]

where f is frequency and d particle diameter. "$\pm\delta$" in Table IV denotes deviation, that is, average deviation value from d_m, which was calculated from

$$\Delta = 1/100 \sum_i (d_m - d_i)^2 f_i$$ [4]

It is obvious from Table IV that variation in form or aggregation of pigment particles did not occur by the treatment of pigments in the aqueous solution of rongalit. Namely, as already described, it was confirmed that the variation of color was due to the change of chemical composition.

Summary

Action of reducing agents on copper phthalocyanine and its chlorinated derivatives was studied, and it was found that, while copper phthalocyanine containing no chlorine did not suffer from discoloration, the color of its polychlorinated derivatives darkened. The discoloration, was most conspicuous when 13 to 14 chlorine atoms per phthalocyanine molecule were contained. The chlorinated copper phthalocyanine become stable towared reducing agents when it was exhaustively chlorinated.

It was confirmed that the darkening of the color of pigments was caused by the change of chemical composition, not by the change of size and form of particles.

The author extends his sincere thanks to Dr. Ryozo Goto, Professor of Kyoto University, for his kind guidance throughout the present study. The author's grateful thanks are also due to Dr. Takahisa Nakamura and Dr. Wataru Ishikawa, Toyo Ink Manufacturing Company, for the valuable advice and much help during the experiments.

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4) E. Suito et al., presented at the 58th Meeting of Electron Microscope Committee of Japan, 1951.

Hydrogen Peroxide Oxidation. I. A New Selenium Dioxide-Catalyzed Synthesis of Carboxylic Acids from Aliphatic Ketones Accompanied by Rearrangement of Alkyl Groups

By Noboru SONODA and Shigeru TSUTSUMI

(Received November 6, 1958)

In the selenium dioxide oxidation of aliphatic carbonyl compounds, α-dicarbonyl compounds are generally obtained, whereas in the presence of hydrogen peroxide the oxidative reaction proceeds quite differently. For instance, selenium dioxide was used as catalyst for hydroxylation of olefins[1,2], and recently the use of selenium dioxide catalyst for the hydrogen peroxide oxidation of acrolein to acrylic acid has been reported by Smith and Holm[3], and the ring contraction of cycloalkanones to cycloalkanecarboxylic acids has also been confirmed by Payne and Smith[4].

We had tried to hydroxylate olefins with hydrogen peroxide in the presence of selenium dioxide catalyst and by using a mixed solvent of *tert*-butyl alcohol and a ketone. It was interesting to note that the oxidation of the ketone, used as solvent, proceeded mainly to form carboxylic acid accompanied by a migration of an alkyl group of the ketone.

For the purpose of elucidating the new reaction mode, acetone, methyl ethyl ketone, methyl *n*-propyl ketone and diethyl ketone were chosen as the starting materials. In the presence of a catalytic

1) M. Mugdan and D. P. Young, *J. Chem. Soc.*, **1949**, 2988.
2) P. Seguin, *Compt. rend.*, **216**, 667 (1943).
3) C. W. Smith and R. T. Holm, *J. Org. Chem.*, **22**, 746 (1957).
4) G. B. Payne and C. W. Smith, ibid., **22**, 1680 (1957).

amount of selenium dioxide, the oxidation of ketones was carried out with a slight excess of hydrogen peroxide in *tert*-butyl alcohol in gentle reflux condition (78~82 °C) for 5~6 hr. At the end of the oxidation the deposition of metallic selenium was observed by which the reaction mixture was colored brownish red, while the hydrogen peroxide completely disappeared. The oxidation products were separated by fractional distillation and analyzed.

When acetone was treated according to the above method, propionic acid, which arose by the shift of either of the methyl carbons to another, was isolated in a yield of 40.7% based on the acetone used. The oxidation of methyl ethyl ketone under similar conditions gave isobutyric acid as the main product in a 27.3% yield and *n*-butyric acid in a 4.8% yield. Both products were formed by the respective migration of the methyl and ethyl groups to the α-carbon atom of the carbonyl group.

$$\mathrm{CH_3}\diagup\mathrm{CH_3}\diagdown\mathrm{C{=}O} \xrightarrow[\textit{tert}\text{-butyl alcohol}]{\mathrm{SeO_2{-}H_2O_2}} \mathrm{CH_3CH_2COOH} \quad (1)$$

$$\mathrm{CH_3CH_2}\diagup\mathrm{CH_3}\diagdown\mathrm{C{=}O} \longrightarrow \mathrm{CH_3}\diagup\mathrm{CH_3}\diagdown\mathrm{CHCOOH} + \mathrm{CH_3CH_2CH_2COOH} \quad (2)$$

All the acids obtained were identified by their physical properties, preparation of the derivatives (*p*-bromophenacyl esters), and their infrared spectra.

When methyl *n*-propyl ketone and diethyl ketone were oxidized under similar conditions to those described above, methyl ethyl acetic acid, which was formed by the respective migration of methyl and ethyl groups to the α-carbon atoms of the carbonyl groups, was isolated in a yield of 22.8% and 32.4%, respectively. The migration of *n*-propyl group of methyl *n*-propyl ketone was also observed, producing *n*-valeric acid in a 5.7% yield.

$$\mathrm{CH_3CH_2CH_2}\diagup\mathrm{CH_3}\diagdown\mathrm{C{=}O} \xrightarrow{\mathrm{SeO_2{-}H_2O_2}} \mathrm{CH_3CH_2}\diagup\mathrm{CH_3}\diagdown\mathrm{CHCOOH} + \mathrm{CH_3CH_2CH_2CH_2COOH} \quad (3)$$

$$\mathrm{CH_3CH_2}\diagup\mathrm{CH_3CH_2}\diagdown\mathrm{C{=}O} \longrightarrow \mathrm{CH_3CH_2}\diagup\mathrm{CH_3}\diagdown\mathrm{CHCOOH} \quad (4)$$

The above results suggest that similar treatments can be applied to other dialkyl ketones. Thus, the oxidative reactions may be generalized as follows;

$$\mathrm{R{-}CH_2}\diagup\mathrm{R'}\diagdown\mathrm{C{=}O} \xrightarrow[\textit{tert}\text{-butyl alcohol}]{\mathrm{SeO_2{-}H_2O_2}} \mathrm{R}\diagup\mathrm{R'}\diagdown\mathrm{CHCOOH} \quad (5)$$

R=H or alkyl R'=alkyl

It is inferable that the main rearrangement in these oxidative reactions is due to the migration of the alkyl group having a smaller number of carbon atoms to the α-carbon atom of the larger alkyl group, and, in consequence, the generated acids have the same number of carbon atoms as the original ketones. On the other hand, the migration of the alkyl group with a larger number of carbon atoms to the smaller one occurs simultaneously in some degree, so that the corresponding isomers are obtainable when unsymmetrical dialkyl ketones are used.

Small amounts of cleavage products were obtained as by-products in all cases. These are listed in Table I.

TABLE I. CLEAVAGE PRODUCTS FROM OXIDATIVE REACTION OF KETONES

Reactants	Products confirmed	Yield
acetone	acetic acid[a]	trace
methyl ethyl ketone	acetic acid	trace
	propionic acid	trace
methyl *n*-propyl ketone	acetic acid[b]	trace
diethyl ketone	acetic acid[a]	trace
	propionic acid	4.1%

(a) The presence of acetic acid was confirmed by the boiling point, the refractive index and the value of neutral equivalent, and the other acids were identified in the form of *p*-bromophenacyl esters.
(b) Propionic acid and *n*-butyric acid are assumed to be present, but were not detected.

These products have apparently formed by the cleavage of the bond between the α-carbon atom and the carbonyl group, although, propionic acid can partly be furnished from oxidation of the solvent; because acetone and methyl alcohol are presumed to be generated from the decomposition of *tert*-butyl hydroperoxide and di-*tert*-butyl peroxide which are produced by the reaction of *tert*-butyl alcohol, used as solvent, with hydrogen peroxide. Actually, the formation of a small amount of aceton was observed (identified as its 2,4-dinitrophenylhydrazone; the melting point and mixed melting point with authentic sample were 123°C[5]) when the

5) W. Dirscherl and H. Nahm, *Ber.*, 73, 448 (1940).

selenium dioxide-hydrogen peroxide solution used above was heated without ketones.

The presence of acetic acid and propionic acid in the oxidation products of diethyl ketone indicates that both of the cleavaged groups from one ketone can be oxidized to acids in these reaction systems. In addition, the occurrence of formic acid due to the cleavage of methyl alkyl ketones or oxidation of methyl alcohol produced from solvent may be possible, but it was not detectable.

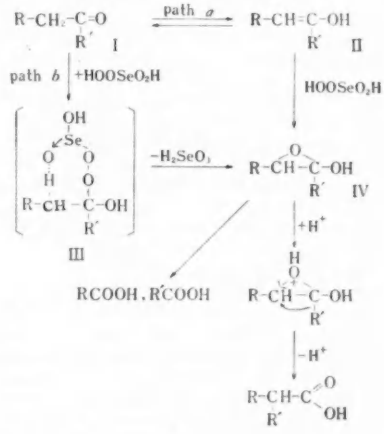
Synthesis of carboxylic acids from ketones by the use of aqueous ammonium polysulfide or a mixture of sulfur and water has been known as Willgerodt-reaction[6], in which aromatic-aliphatic ketones are mainly used as the starting materials, and no change of the carbon skeleton has been observed because of the consecutive reduction and oxidation of the carbon atoms in the aliphatic carbon chain. In the reaction described here the rearrangement of alkyl group occurs apparently and therefore the reaction mode is different from the Willgerodt-reaction. On the other hand, oxidation of ketones accompanying the rearrangement of alkyl group, by peracids or hydrogen peroxide in the presence of acidic catalyst, has been well known as Baeyer-Villiger reaction[7], but in this case the migrating alkyl group becomes the ester group of the resulting carboxylic acid so that the carbon numbers of the generated carboxylic acid are less than those of the starting ketone used. It is of interest to note that the rearrangement by the selenium dioxide-hydrogen peroxide system is applicable to such lower ketones as acetone and methyl ethyl ketone which produce monomeric or polymeric ketone-peroxides under the conditions of Baeyer-Villiger reaction. The ring contraction of cycloalkanones reported by Payne and Smith[4] may be interpreted as one of the rearrangement reactions described here.

Although little evidence was obtained about the mechanism of the rearrangement, the reaction would obviously proceed owing to the peculiar action of the catalyst. It seems to us that selenium dioxide may not affect the reaction directly but a further oxidized form of selenium dioxide by hydrogen peroxide may be the most probable catalytic form. Because α-dicarbonyl compound is not the intermediate[4]; for example, diacetyl was cloven into two molecules of acetic acid under the same reaction conditions and C_4-acid was not obtained.

The oxidation of selenium dioxide with hydrogen peroxide has been reported by several workers[8-10]. Hughes and Martin[9] proposed the formation of peroxyselenious acid in the course of the oxidation of selenium dioxide to selenic acid as shown below.

$$SeO_2 + H_2O_2 \rightleftarrows HOOSeO_2H$$

We investigated[11] previously the fact that the hydroxylation of a double bond was possible by applying the same oxidative method to olefins, and this fact would be elucidated by considering the formation of some kind of peracid in the reaction system. In the present case, the peroxyselenious acid may be formed in *tert*-butyl alcohol solution and may attack ketones in an ionic fashion; thus the following mechanism will be presumed.



Path a indicates that the epoxidation of *enol*-form II by the peroxyselenious acid may occur and addition of proton to the resulting epoxyalcohol IV may cause the migration of an alkyl group. Formation of epoxyalcohol IV will be also expected

6) For a review of this reaction, see (a) M. Carmack, "Organic Reactions", Vol. III, John Wiley and Sons, Inc., New York, N. Y.(1946), p. 83-107; (b) R. Wegler, E. Kühle and W. Schäfer, *Angew. Chem.*, **70**, 351 (1958).

7) For a review of this reaction, see C. H. Hassall, "Organic Reactions", Vol. IX, John Wiley and Sons, Inc., New York, N. Y. (1957), p. 73-106.

8) L. I. Gilbertson and G. B. King, *J. Am. Chem. Soc.*, **58**, 180 (1936).

9) F. J. Hughes and D. S. Martin, Jr., *J. Phys. Chem.*, **59**, 410 (1955).

10) B. Maliňák, *Chem. Listy.*, **50**, 160 (1956); *Chem. Abstr.*, **50**, 3939*a* (1956).

11) The results were presented at the 11th Annual Meeting of the Chemical Society of Japan held in Tokyo, April 3, 1958.

from path b which may include the combination between the α-hydrogen and the oxygen of peroxyselenious acid at the same time of addition of peroxyselenious acid to the carbonyl group. The former path would be more favorable to the latter because of the difficulty of such ring formation III. After the epoxidation, the peroxyselenious acid may become selenious acid which is in equilibrium with selenium dioxide and water (equation 7)[9],

$$H_2SeO_3 \rightleftharpoons SeO_2 + H_2O \qquad (7)$$

and the reproduced selenium dioxide will be again oxidized to peroxyselenious acid with hydrogen peroxide (equation 6).

Experimental[12]

Starting Materials.—The ketones and the solvent used in this study were commercial products. Acetone and methyl ethyl ketone were carefully purified by treatment with potassium permanganate solution according to the usual method[13]. The other ketones and *tert*-butyl alcohol, used as the solvent, were purified by fractional distillation prior to their uses. Hydrogen peroxide (30%) and selenium dioxide were from Wako Pure Chemical Industries, Ltd.

Reagent for Oxidation.—A solution containing 150 ml. of 30% hydrogen peroxide and 600 ml. of *tert*-butyl alcohol was dried over 200 g. of anhydrous sodium sulfate overnight. After separating the sodium sulfate, the concentration of hydrogen peroxide in the solution was determined by iodometry. A solution containing 68~69 mg. of hydrogen peroxide per 1 ml. was obtained, and 2 g. of selenium dioxide was dissolved in 500 ml. of the solution (corresponding to about 1 mol. of hydrogen peroxide) with stirring. Selenium dioxide-hydrogen peroxide reagent thus obtained was used in all experiments.

Oxidation of Acetone.—A 1 l. round bottomed flask was charged with 500 ml. of the selenium dioxide-hydrogen peroxide reagent (2 g. of selenium dioxide and 1 mol. of hydrogen peroxide), and 50 g. (0.86 mol.) of acetone was added slowly with stirring. The flask was then fitted with an efficient reflux condenser and was heated on a steam bath. After refluxing (79~81°C) the mixture gently for about 5 hr., the solution became brownish red owing to the deposition of metallic selenium, and the hydrogen peroxide had been completely consumed at this stage. The reaction mixture was allowed to cool to room temperature, the reflux condenser was exchanged for a Widmer-spiral and the distillation was then carried out to remove the remaining acetone-*tert*-butyl alcohol azeotropic mixture. When about 400 ml. of the azeotropic mixture was distilled off, the residue was cooled and the precipitated metallic selenium was filtered off. Ten g. of anhydrous sodium sulfate and 50 ml. of ether were added to the filtrate. After the solution was allowed to stand overnight, it was transferred to a separatory funnel and the water layer was removed and dried over anhydrous sodium sulfate. The ether and the products boiling up to 83°C were distilled off and materials of higher boiling point were fractionated through a 1×40 cm. packed column. The fraction boiling at 139.5~141°C was collected, and 26.0 g. of propionic acid was obtained (40.7% of the theoretical amount based on the quantity of acetone used); n_D^{25} 1.3852, neut. equiv. 74.8; lit.[14] b. p. 140.3°C, n_D^{25} 1.3848. Calcd. for $C_3H_6O_2$: neut. equiv. 74.1.

The infrared spectrum of the acid coincided with that of an authentic sample. *p*-Bromophenacyl ester of the acid was prepared by an usual method[15], m. p. 63.5~64°C, reported[16] 63°C. The mixed melting point with an authentic sample (63.5~64°C) was not depressed.

Anal. Found: C, 48.64; H, 4.23%. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.74; H, 4.09%.

The results of fractional distillation and the characterization of each fraction were listed in Table II.

Table II. Distillation of oxidation products from acetone

Fraction	B. p. °C	Vol. ml.	Characterization n_D^{25}	neut. equiv.
a-1	82~108	6.0	1.3738	90.2
a-2	108~115	2.0	1.3721	69.2
a-3	115~125	0.5	1.3781	78.5
a-4	125~135	0.6	1.3810	83.7
a-5	135~138	o.5	1.3822	80.0
a-6	138~139.5	0.9	1.3844	78.9
a-7	139.5~141	26.0	1.3852	74.8
	residue	1.7(g.)		

Fraction a-1 contained small amount of azeotropic mixture of acids and water. From the value of neutral equivalent, fraction a-2 seemed to contain the carboxylic acid lower than propionic acid. The *p*-bromophenacyl ester of fraction a-2 had melting point of 79~105°C, which indicated presumably the presence of formic acid and acetic acid: reported melting point of *p*-bromophenacyl ester of acetic acid, 85°C[16]; *p*-bromophenacyl ester of formic acid, 135°C[15]. It was presumed from the value of neutral equivalent that fraction a-3 was acetic acid which was contaminated by impurities other than carboxylic acid. Fraction a-4 was also an acid component but was contaminated by impurities. *p*-Bromophenacyl ester of fractions a-5 and a-6 were confirmed to be that of propionic acid

12) The boiling and melting points are uncorrected.
13) A. Weissberger and E. S. Proskauer, "Organic Solvents", Interscience Publishers, Inc., New York, N.Y. (1955).
14) H. U. v. Vogel, "Chemiker Kalender", Springer-Verlag OHG., Berlin (1956).
15) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 4th ed., John Wiley and Sons, Inc., New York, N. Y. (1956).
16) W. L. Judefind and E. E. Reid, *J. Am. Chem. Soc.*, **42**, 1043 (1920).

respectively from their melting points and mixed melting points with an authentic sample. Fraction a-7 was propionic acid, and the residue in the distilling flask consisted mainly of metallic selenium.

Oxidation of Methyl Ethyl Ketone. — To a 500 ml. of the selenium dioxide-hydrogen peroxide reagent (2 g. of selenium dioxide and 1 mol. of hydrogen peroxide) was added 62g. (0.86 mol.) of a methyl ethyl ketone, and the reaction was carried out under gentle reflux condition for 5.5 hr. The reaction mixture was concentrated through a Widmer-spiral to about 150 ml., and conducted in the same manner as described for the oxidation of acetone. The results of the fractional distillation were listed in Table III.

TABLE III. DISTILLATION OF OXIDATION PRODUCTS FROM METHYL ETHYL KETONE

Fraction	B. p. °C	Vol. ml.	Characterization n_D^{25}	neut. equiv.
b-1	102~115	1.0	1.3715	80.7
b-2	115~121	1.0	1.3756	67.7
b-3	121~137	0.4	1.3799	73.0
b-4	137~142	0.5	1.3838	77.4
b-5	142~152	1.2	1.3904	85.5
b-6	152~153.5	1.8	1.3923	88.1
b-7	153.5~156.5	21.2	1.3928	88.9
b-8	156.5~162	2.3	1.3950	89.2
b-9	162~164	4.1	1.3965	88.3
	residue	1.8(g.)		

Fraction b-1 consisted principally of the azeotropic mixture between lower carboxylic acids and water from the standpoint of the values of neutral equivalent and the refractive idex. Fraction b-2 was acetic acid which was identified, from its *p*-bromophenacyl ester m. p. 84~84.5°C; reported[16] m. p. 85°C; the depression of melting point was not shown when the ester was mixed with an authentic sample (m. p. 84.5°C).

Fraction b-3 would be possibly a mixture of acids. Fraction b-4 was identified to be propionic acid from the melting point of its *p*-bromophenacyl ester, m. p. 62.5~63°C, reported[16] m. p. 63°C; the mixed melting point with an authentic sample was not depressed. Fraction b-5 would be a mixture of acids. Fractions b-6 and b-7 were isobutyric acid, 23 g. (27.3% yield of the theoretical amont based on the quantity of methyl ethyl ketone used); the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p. 154.6°C, n_D^{20} 1.3930; Calcd. for $C_4H_8O_2$, neut. equiv. 88.1.

p-Bromophenacyl ester of the acid was prepared, m. p. 75~75.5C°, reported[16] m. p. 76.2°C. The mixed melting point with an authentic sample (m. p. 75.5°C) was not depressed.

Anal. Found: C, 50.68; H, 4.59. Calcd. for $C_{12}H_{13}O_3Br$: C, 50.55; H, 4.60%.

Fraction b-8 would be obviously a mixture of isobutyric acid and *n*-butyric acid.

Fraction b-9 was *n*-butyric acid, 4.1 g. (4.8% yield based on the quantity of methyl ethyl ketone used); the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p, 164°C, n_D^{20} 1.3979; Calcd. for $C_4H_8O_2$, neut. equiv. 88.1.

p-Bromophenacyl ester of the acid was prepared, m. p. 62.5°C reported[16] m. p. 63°C. The mixed melting point with an authentic sample (62.5°C) was not depressed.

Anal. Found: C, 50.39; H, 4.70. Calcd. for $C_{12}H_{13}O_3Br$: C, 50.55; H, 4.60%.

Oxidation of Methyl *n*-Propyl Ketone. — To a 250 ml. (1 g. of selenium dioxide and 0.5 mol. of hydrogen peroxide of the selenium dioxide-hydrogen peroxide reagent was added 37 g. (0.43 mol.) of a methyl *n*-propyl ketone, and the mixture was treated under the gentle reflux condition for 6 hr. The reaction mixture was concentrated through a Widmer-spiral to about 70 ml. (when aqueous layer had separated) followed by addition of 5 g. of anhydrous sodium sulfate to saturate the aqueous layer. After separation, the aqueous layer was extracted with 20 ml. of ether. A mixture of the ether extract and the separated organic layer was dried over anhydrous sodium sulfate, and fractional distillation was carried out through the same column described as in the case of acetone. The results of the fractional distillation were listed in Table IV.

TABLE IV. DISTILLATION OF OXIDATION PRODUCTS FROM METHYL *n*-PROPYL KETONE

Fraction	B. p. °C	Vol. ml.	Characterization n_D^{25}	neut. equiv.
c-1	110~117	0.9	1.3733	67.5
c-2	117~122	0.3	1.3752	—
c-3	122~160	1.3	1.3875	81.3
c-4	160~166	0.4	1.3977	97.2
c-5	166~172	1.0	1.4008	101.3
c-6	172~175	3.1	1.4030	103.0
c-7	175~177	7.5	1.4044	103.7
c-8	177~182	1.1	1.4059	102.8
c-9	182~186	2.7	1.4074	104.0
	residue	2.2(g.)		

Fraction c-1 would be a mixture of lower carboxylic acids which consisted mostly of acetic acid. Fraction c-2 was identified as acetic acid from its *p*-bromophenacyl ester, m. p. 84.5°C, reported[16] 85°C; the mixed melting point with an authentic sample was not depressed. Fractions c-3 and c-4 would be a mixture of acids, and a detectable amount of *n*-butyric acid was not obtained. The greater part of fraction c-5 would consist of methyl ethyl acetic acid similar to the next fraction.

Fractions c-6 and c-7 were identified to be methyl ethyl acetic acid, 10.0 g. (22.8% yield of the theoretical amount based on the methyl *n*-propyl ketone used), the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p. 174°C (reported[15] 176°C), n_D^{20} 1.4051; Calcd. for $C_5H_{10}O_2$, neut. equiv. 102.1.

17) O. T. Schmidt, *Ann.*, **483**, 115 (1930).

p-Bromophenacyl ester of the acid was prepared from the fraction c-7, m. p. 54.5~55°C, reported[15] 55°C; mixed melting point with an authentic sample was not depressed.

Anal. Found: C, 52.34; H, 5.36. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.19; H, 5.06%.

Fraction c-9 was confirmed to be *n*-valeric acid, 2.5 g. (5.7% yield based on the ketone used); the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p. 186.4°C, n_D^{20} 1.4086; Calcd. for $C_5H_{10}O_2$, neut. equiv. 102.1.

p-Bromophenacyl ester of the acid was prepared; m. p. 73.5~74°C, reported[17] m. p. 74°C; the mixed melting point with an authentic sample was not depressed.

Anal. Found: C, 52.01; H, 5.33. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.19; H, 5.06%.

Oxidation of Diethyl Ketone.—To a 150 ml. (0.6 g. of selenium dioxide and 0.3 mol. of hydrogen peroxide) of selenium dioxide-hydrogen peroxide reagent was added 22.4 g. (0.26 mol.) of diethyl ketone, and the mixture was gently refluxed for 5.5 hr. The resulting reaction mixture was concentrated through a Widmer-spiral to about 50 ml. and was treated according to the same method as described in the case of methyl *n*-propyl ketone. The results of the fractional distillation were listed in Table V.

TABLE V. DISTILLATION OF OXIDATION PRODUCTS FROM DIETHYL KETONE

Fraction	B. p.	Vol.	Characterization	
	°C	ml.	n_D^{25}	neut. equiv.
d-1	103~112	1.2	—	—
d-2	112~124	0.5	1.3770	68.4
d-3	124~135	0.3	—	—
d-4	135~142	0.8	1.3860	75.4
d-5	142~160	0.6	1.3891	82.8
d-6	160~170	0.5	1.3960	91.0
d-7	170~174	0.8	1.4033	101.5
d-8	174~177	8.0	1.4040	103.1
d-9	177~179	0.3	1.4051	104.8
	residue	1.1(g.)		

Fraction d-1 was an azeotropic mixture of acids and water. Fraction d-2 was a mixture of acids which would consist mainly of acetic acid from the standpoint of the boiling range, the refractive index and the value of neutral equivalent, but the *p*-bromophenacyl ester did not give the constant melting point owing to the presence of the ester of the other acids. Fraction d-3 would be a mixture of acetic acid and propionic acid.

Fraction d-4 was identified to be propionic acid (4.1% yield based on the ketone used); *p*-bromophenacyl ester, m. p. 62.5~63.5°C, reported[16] m. p. 63°C, the mixed melting point with an authentic sample was not depressed. Fractions d-5 and d-6 would be a mixture of acids which were not identified.

Fractions d-7 and d-8 were identified to be methyl ethyl acetic acid, 8.6 g. (32.4% yield based on the quantity of diethyl ketone used); the infrared spectra of these fractions coincided with that of an authentic sample; lit.[14] b. p. 174°C (reported[15] 176°C); n_D^{20} 1.4051; Calcd. for $C_5H_{10}O_2$, neut. equiv. 102.1.

p-Bromophenacyl ester was prepared from the fraction d-8, m. p. 55°C, reported[15] m. p. 55°C; the mixture melting point with an authentic sample was not depressed.

Anal. Found: C, 51.94; H, 5.06. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.19; H, 5.06%.

Oxidation of Diacetyl.—To a 130 ml. (0.52 g. selenium dioxide and 0.26 mol. hydrogen peroxide) of the selenium dioxide-hydrogen peroxide reagent was added 21.5 g. (0.25 mol.) of diacetyl. The mixture was refluxed for 6.5 hr. and then was treated in the same manner as described for the oxidation of acetone. Acetic acid (b. p. 117~119°C) was isolated by distillation and the yield was 10.8 g. (36.0% based on diacetyl used).

Summary

1) Selenium dioxide catalyzed oxidation of aliphatic ketones with hydrogen peroxide gave carboxylic acids which were produced by the rearrangement of the alkyl group as shown by equation 5.

2) Acetone, methyl ethyl ketone, methyl *n*-propyl ketone and diethyl ketone were selected as starting materials. The main rearrangement observed is due to the migration of the alkyl group having a smaller number of carbon atoms to the *α*-carbon atom of the larger alkyl group, and the migration of the alkyl group with a larger number of carbon atoms to the smaller one also occurs in some degree.

3) The yield of the generated acids were about 30~40% of the theoretical amounts based on the ketones used. Small amounts of cleavage products were obtained as the by-products in all cases. Both of the cleavaged groups from a ketone were oxidized to acids in these reaction systems.

4) The most probable catalytic form seems to be peroxyselenious acid which may be produced by the oxidation of selenium dioxide with hydrogen peroxide (equation 6). Inferential reaction mechanism was discussed.

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Protonation Effects on the Electronic Spectra of Pyrazine

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In our previous reports[1,2], we have tried to interpret theoretically the characteristics of electronic spectra of hydrogen bonded or protonated nitrogen heterocycles, especially in the case of pyridine. In these reports, semiempirical Hartree-Fock SCF MO's for pyridine interacting with proton have been computed assuming extreme models: (1), there is no transfer of non-bonding electrons on nitrogen toward proton, but bare proton or somewhat shielded proton is located near the nitrogen atom of neutral molecules. In the latter case, the effective charge of proton has been introduced in theory (model I); (2), there is considerable charge transfer from nitrogen atom to proton, leading to covalent binding between them (model II).

The calculated sepectra with model I were in a very good agreement with the experiment. The calculation with model II, however, led to a result which gave rather poor agreement with the experimental values. These results were examined carefully and some discussions on the cause of the superiority of model I and the unsatisfactory result obtained with model II were given.

In the present paper, we shall report another example of our calculations, i.e., the study of the electronic spectra of pyrazinium diion. In this case, the features of spectral change produced by protonation are somewhat different from the case of pyridine.

Method of Calculation

Our method of calculation has already been described in detail elsewhere[2]. Accordingly, the outline of our method will be given briefly as follows.

Model I.—In this case, the complete electronic Hamiltonian may be written as,

$$H=\sum_i H_i^{c\ rel}+\sum_{i<j}^{2m}(e^2/r_{ij}) \tag{1}$$

$$H_i^{core\dagger}=H_i^{core}+H_i^P \tag{2}$$

where H_i^P is the electrostatic potential due to proton

$$H_i^P=-\sum_P\frac{Z_{H^+}e^2}{r_{Pi}} \tag{3}$$

In Eq. 2, r_{Pi} is the distance between proton and i-th electron and $Z_{H^+}e$ is the effective charge of proton. In the present calculation it has been assumed to be $Z_{H^+}=1$. The i-th MO may be written in the LCAO form as,

$$\phi_i=\sum_\mu C_{i\mu}\phi_\mu \tag{4}$$

and the eigenvalue equations become as follows in terms of Hartree-Fock SCF MO with neglect of differential overlap,

$$\sum_\nu F_{\mu\nu}C_{i\nu}=\varepsilon C_{i\mu} \tag{5}$$

where

$$F_{\mu\mu}=\alpha_\mu'+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu}+\sum_{\kappa(\neq\mu)}(P_{\kappa\kappa}-1)\gamma_{\mu\kappa} \tag{6}$$

$$F_{\mu\nu}=B_{\mu\nu}-\frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \tag{7}$$

$$\alpha_\mu'=\alpha_\mu+V_\mu^P \tag{8}$$

$$V_\mu=-\sum Z_{H^+}e^2\int\frac{\phi_\mu^2(i)}{r_{Pi}}\mathrm{d}v(i) \tag{9}$$

The meaning of the quantities in these equations other than V_μ^P is the same as before[3-5]. Among the molecular integrals that arise, V_μ^P has been computed theoretically employing the usual Slater $2p\pi$ AO's of nitrogen and carbon atoms, and the others have been evaluated by the same procedure as before[3-5]. Because the interatomic distances in pyrazinium diion necessary for the evaluation of molecular integrals are uncertain, C–C and C–N distances have been assumed to be the same as in neutral molecules and the N–H$^+$ distance has been put to be 1.032 Å, which is the value determined by Bersohn and Gutowsky[6] by means of nuclear

1) N. Mataga and S. Tsuno, *Naturwiss.*, **45**, 333 (1958).
2) S. Mataga and N. Mataga, *Z. physik. Chem. N. F.*, in press.
3) N. Mataga and K. Nishimoto, ibid., **13**, 140 (1957).
4) N. Mataga, This Bulletin, **31**, 453, 459, 463 (1958).
5) N. Mataga, *Z. physik. Chem. N. F.*, **18**, 285 (1958).
6) R. Bersohn and H. S. Gutowsky, *J. Chem. Phys.*, **22**, 651 (1954).

magnetic resonance in the case of ammonium chloride.

Model II.—For the calculation to be made by this by this model, the values of the valence state ionization potential I_{N^+} and electron affinity A_{N^+} of N^+ ion are needed. Using the values of valence state energies above the ground state, which have been taken from Pritchard and Skinner[7], the values of I_{N^+} and A_{N^+} are easily obtained considering the processes,

$N^+(sp_xp_yp_z,\ V_4) \rightarrow N^{++}(sp_xp_y,\ V_3)$ and

$N(sp_xp_yp_z^2,\ V_3) \rightarrow N^+(sp_xp_yp_z,\ V_4)$,

respectively.

With these values the evaluation of molecular integrals has been made in the same manner as before[1-5], and the salf-consistent field calculation has been worked out.

Results and Discussion

The calculated SCF MO's, MO energies, charge and bond orders are collected in Table I.

TABLE I. SCF MO's, MO ENERGIES, CHARGE AND BOND ORDERS OF PYRAZINIUM DIION

Symmetry	ε_i(eV.)	Model I
b_{2u}	−27.0147	$\phi_1=0.3132(\phi_2+\phi_3+\phi_5+\phi_6)+0.5512(\phi_1+\phi_4)$
b_{3g}	−25.4415	$\phi_2=0.2065(\phi_2-\phi_3-\phi_5+\phi_6)+0.6439(\phi_1-\phi_4)$
b_{1g}	−21.4068	$\phi_3=0.5000(\phi_2+\phi_3-\phi_5-\phi_6)$
b_{2u}	−14.1191	$\phi_4=0.3897(\phi_2+\phi_3+\phi_5+\phi_6)-0.4429(\phi_1+\phi_4)$
a_{1u}	−12.0237	$\phi_5=0.5000(\phi_2-\phi_3+\phi_5-\phi_6)$
b_{3g}	− 9.8972	$\phi_6=0.4553(\phi_2-\phi_3-\phi_5+\phi_6)-0.2920(\phi_1-\phi_4)$

$P_{11}=1.4370,\ P_{22}=0.7815,\ P_{12}=0.6112,\ P_{23}=0.6109$

Symmetry	ε_i(eV.)	Model II
b_{2u}	−20.8925	$\phi_1=0.2038(\phi_2+\phi_3+\phi_5+\phi_6)+0.6457(\phi_1+\phi_4)$
b_{3g}	−20.2163	$\phi_2=0.1425(\phi_2-\phi_3-\phi_5+\phi_6)+0.6778(\phi_1-\phi_4)$
b_{1g}	−10.4320	$\phi_3=0.5000(\phi_2+\phi_3-\phi_5-\phi_6)$
b_{2u}	− 4.6592	$\phi_4=0.4566(\phi_2+\phi_3+\phi_5+\phi_6)-0.2882(\phi_1+\phi_4)$
a_{1u}	− 1.1677	$\phi_5=0.5000(\phi_2-\phi_3+\phi_5-\phi_6)$
b_{3g}	0.3512	$\phi_6=0.4792(\phi_2-\phi_3-\phi_5+\phi_6)-0.2015(\phi_1-\phi_4)$

$P_{11}=1.7526,\ P_{22}=0.6237,\ P_{12}=0.4564,\ P_{23}=0.5425$

As shown in Table I, the charge density at nitrogen is increased remarkably by protonation and the features of charge distribution in neutral pyrazine molecule[3] which can be practically regarded as slightly perturbed benzene[5] are lost. With these MO's and MO energies, the electronic spectra of pyrazinium diion are easily calculated. In Table II the calculated spectra are indicated together with the experimental values.

TABLE II. CALCULATED AND OBSERVED SPECTRA OF PYRAZINIUM DIION

Symmetry	Excitation energy (eV.) Calcd. I	Calcd. II	Obsd.[a]	Oscillator strength Calcd. I	Calcd. II	Obsd.
$^1B_{3u}(^1L_b)$	4.2649	3.6205	4.35	0.489	0.723	*
$^1B_{1u}(^1L_a)$	6.3592	6.3130	(6≦)[b]	0.340	0.504	—
$^1B_{1u}(^1B_a)$	8.0161	11.3617	—	0.659	0.286	—
$^1B_{3u}(^1B_b)$	9.3522	14.2097	—	0.720	0.368	—

(a) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 712 (1951) and S. Mataga, unpublished.

(b) There is no indication of the existence of other electronic band than ^1L_b below 45 *kK*.

* The observed oscillator strength of pyrazinium diion is uncertain. The oscillator strength of ^1L_b band, however, seems to be two or three times as large as that of neutral molecule.

In contradistinction to the case of protonated pyridine, ^1L_b band is somewhat strengthened as well as shifted to red, while the wave length of ^1L_a band seems to remain almost invariable by double protonation. As shown in Table II, the calculated excitation energy with model I is in good agreement with the experiment. In addition to this, since the calculated oscillator strength of ^1L_b band in neutral pyrazine molecule is 0.162[3], the calculated value in Table II, 0.489, is correct in its order of magnitude in comparison with the calculated value of the neutral molecule. In contrast with the satisfactory results obtained by model I, the calculation with model II leads to the result which is in rather poor agreement with the experiment, that is, the calculated red shift and increase of intensity in the case of ^1L_b band are too great compared with the experiment.

As has already been pointed out in the case of protonated pyridine[1,2], the most predominant factor which leads to the unsatisfactory results with model II may be the neglect of the inductive charge displacement in the σ-core, caused by the transfer of non-bonding electrons on the nitrogen atom toward proton. In the case of model II, the core potential is very deep at nitrogen and is the same as

7) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

that in the neutral molecule at the carbon atoms. In the case of model I, however, the difference between the core energies at nitrogen and carbon is not so great as in model II and the displacement in σ-core may be appropriately taken into consideration by the formal use of the electrostatic proton potential.

Moreover, the values of $F_{\mu\mu}$'s which may be regarded as an effective electronegativity of μ atom in the molecule[2,3], show the same tendency as the core energies. They are collected in Table III.

TABLE III. VALUES OF α_μ'S AND $F_{\mu\mu}$'S

Model	F_{11}	F_{22}	α_1'	α_2'
I	−22.3721	−16.2897	−29.0877	−21.9661
II	−18.3705	−5.0689	−28.72	−11.42

Although the observed spectra can be satisfactorily reproduced by model I as described above, one should not regard model I as the real state of protonated pyrazine. This model represents the electric interaction between proton and π-electrons rather than the electronic interaction between proton and pyrazine. The strong charge transfer interaction between the nitrogen atom in pyrazine and proton may lead to a fairly strong covalent binding between them. Then, the changes in the core energies produced by protonation may be almost completely contributed by the inductive displacement in σ-core. If this is the case, in view of the short range character of the interactions in σ-core, the $(\alpha_\mu'-\alpha_\mu)$ values used in the calculation with model I may be too large. It seems probable that the protonation effect on the core energies may be almost negligible at the nitrogen atom in the opposite side of that proton. However, if we use $(V_\mu'-2V_0')$'s instead of V_μ''s of Eq. 9, where V_0' is the potential energy due to proton at the nitrogen atom in the opposite side of that proton, it is evident that the MO's calculated by model I stay unchanged although the MO energies are lifted by $2|V_0'|$ uniformly. Thus, the calculation with model I may still be correct even in this case. One might be able to say that the real changes in core energies due to inductive displacement are approximately represented by $(V_\mu'-2V_0')$ in the case of doubly protonated pyrazine. We shall give a detailed and critical discussion in a later report[8] about such a statement comparing the results obtained with model I with those obtained by an improved model II which employs the self-consistent electronegativity method as developed by Brown and Heffernan[9].

Summary

The protonation effect on the electronic structure and spectra of pyrazine has been studied theoretically employing quantum mechanical calculation. Semi-empirical Hartree-Fock SCF MO's for pyrazine interacting with two protons have been computed with two different methods, respectively.

i) Electrostatic potential due to proton has been added to the core potential in the total electronic Hamiltonian and nuclear attraction integrals which arise owing to the proton potential have been computed theoretically employing the usual Slater $2p\pi$ AO's.

ii) The doubly protonated pyrazine has been replaced by doubly charged pyrazinium ion and molecular integrals have been evaluated semi-empirically using valence state ionization potential and electron affinity of the N^+ atom.

The calculated spectra with method i are in a very good agreement with the experiment. The calculation with method ii has led to a result which is in rather poor agreement with the experimental observation. On the basis of these results, some discussions about the protonation effect on the electronic structure of this molecule have been given.

We are grateful to Professor R. Fujishiro for his encouragement throughout the present study. We also express our appreciation to Mr. T. Kubota of Shionogi Co., Ltd. for his helpful discussions.

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8) S. Mataga and N. Mataga, to be published elsewhere.

9) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

Intramolecular Cyclization of o,o'-Dihydroxydiphenyldiacetylene

By Fumio TODA and Masazumi NAKAGAWA

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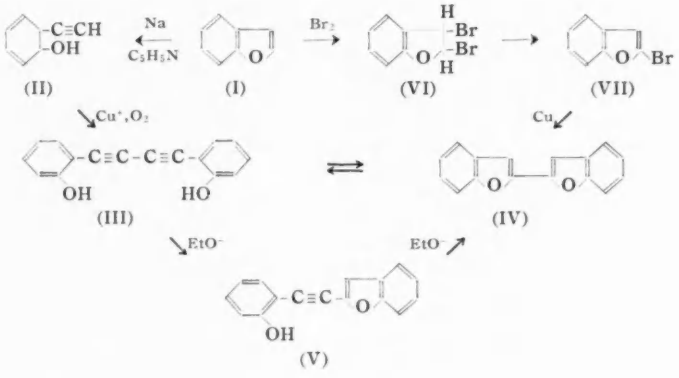
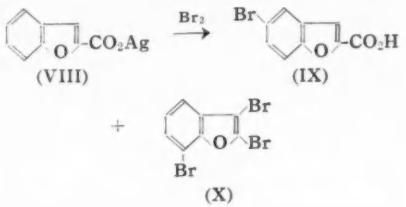
Recently the reactivity of acetylenic bond to the variety of nucleophilic reagents is well recognized, and the formation of furane ring by the intramolecular cyclization of acetylenic glycol[1] and acetylenic phenol[2] has been reported by several investigators. In the course of the studies concerning the synthesis of cyclic acetylenic compounds, the authors found that the nucleophilic addition of the hydroxyl groups in *o,o'*-dihydroxydiphenyldiacetylene (III) to the triple bonds in the same molecule yields benzofurane derivatives. The present paper reports the formation and the structure determination of the benzofurane derivatives thus obtained.

o-Hydroxyphenylacetylene (II) was prepared according to the method of Prey[3] cleaving the furane ring in coumarone I with sodium in pyridine. Oxidative coupling of II was carried out according to the procedure of Sörensen[4] yielding *o,o'*-dihydroxydiphenyldiacetylene (III) in good yield. The physical properties of III were identical with those of the previously reported values[5]. III was heated on a water bath for a few hours with diluted ethanolic sodium ethoxide solution or with aqueous sodium hydroxide solution forming a neutral material in quantitative yield. The U. V. and I. R. spectra of this substance indicate the absence of any acetylenic linkage and hydroxyl group. The presence of ether linkage was recognized from the characteristic absorption at 1250 cm^{-1}. The neutral material yielded III and an unidentified phenolic polymerized material on the treatment with sodium in pyridine at 160~170°C. From these findings the structure of 2,2'-dibenzofuranyl (IV) was assigned to the neutral material. This assignment was confirmed by the mixed melting point determination of the neutral material with a synthetic specimen which was obtained by the Ullmann reaction of 2-bromobenzofurane (VII). VII was prepared by the pyrolytic distillation of 2,3-dibromocoumarane (VI)[6]. The attempt to prepare VII by the Hunsdiecker reaction of silver coumarilate VIII gave an unsatisfactory result. The products were found to be 5-bromocoumarilic acid (IX)[7] and so-called 2,3,7(?)-tribromocoumarone (X)[8].



1) G. Dupont, R. Dulou and L. Audier, *Bull. soc. chim. France*, **1955**, 1078.
2) W. Ried, *Angew. Chem.*, **70**, 273 (1958).
3) V. Prey and G. Pieh, *Monatsh. Chem.*, **80**, 790 (1949).
4) T. Bruun, T. Morthei and N. A. Sörensen, *Acta Chem. Scand.*, **4**, 850 (1950).
5) Y. Odaira, This Bulletin, **29**, 470 (1956).
6) R. Stoermer and B. Kahlert, *Ber.*, **35**, 1633 (1902).
7) R. Stoermer, *Ann.*, **312**, 237 (1900).
8) R. Stoermer and G. Calov, *Ber.*, **34**, 770 (1901).



A phenolic substance and IV was obtained when III in ethanol was refluxed for 1.5 hr. with a small amount of sodium ethoxide. The I. R. spectrum of the phenolic substance showed the characteristic absorption bands of acetylenic bond and hydroxyl group at 2207 cm^{-1} and 3380 cm^{-1} respectively. This substance was converted into IV quantitatively by the action of alkali. It is reasonable to conclude that the structure of the phenolic substance is 2-(*o*-hydroxyphenylethynyl)-benzofurane (V) formed by the half ring closure of III.

Experimental*

***o*, *o'*-Dihydroxydiphenyldiacetylene (III).**—*o*-Hydroxyphenylacetylene[3] (II, 23.6 g.) was mixed with cuprous chloride (14.5 g.), ammonium chloride (225 g.), concentrated aqueous ammonia 4.0 cc.) and water (572 cc.). The mixture was vigorously stirred at room temperature under an atomosphere of oxygen. The exothermic reaction was completed during the period of 6 hr. with the absorption of theoretical amount of oxygen. The reaction mixture was extracted with ether, washed with water and dried over anhydrous magnesium sulfate. The crude crystals obtained by the evaporation of the solvent were recrystallized from carbon tetrachloride yielding 23 g. (86%) of III, m. p. 142~143°C, colorless needles.

Anal. Found: C, 81.99; H, 4.30. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

U. V. max., 258, 276, 316 and 346 mμ (log ε = 4.13, 3.85, 4.55 and 4.39). I. R. max., 3300, 2180 and 1190 cm^{-1}.

Reaction of III with benzoyl chloride gave dibenzoyl derivative, m. p. 126~126.5°C (from ethanol), colorless needles.

Anal. Found: C, 81.58; H, 4.30. Calcd. for $C_{30}H_{18}O_4$: C, 81.43; H, 4.10%.

U. V. max., 230, 275, 311 and 332 mμ (log ε = 4.91, 4.36, 4.54 and 4.48). I. R. max., 2200, 1744, 1260 and 1240 cm^{-1}.

2, 2'-Dibenzofuranyl (IV) —III (1.0 g.) was dissolved in 30 cc. of 10~20% solution of sodium ethoxide in ethanol or of sodium hydroxide in water. No change was observed after keeping the solution overnight at room temperature. The solution was heated on a water bath for 1~2 hr. causing deposition of crystals. The cooled reaction mixture was filtered. Recrystallization from benzene or ethanol gave IV as colorless needles, m. p. 194.5~195.5°C in quantitative yield.

Anal. Found: C, 81.94; H, 4.47. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

U. V. max., 320 and 338 mμ (log ε = 4.77 and 4.77). I. R. max., 1250 and 1170 cm^{-1}.

Synthesis of 2, 2'-Dibenzofuranyl (IV).—An intimate mixture of 2-bromocoumarone (VII, 1.0 g.) and activated copper bronze (2.5 g.) was heated to 225~240°C in an oil bath for 5 hr. The cooled reaction mixture was transferred to a sublimation apparatus, and was heated to 160~180°C at 20 mmHg. Colorless crystals were obtained as sublimate after removal of the unreacted VII. The crystals were recrystallized from ethanol giving 0.2 g. (40%) of colorless needles, m. p. 194.5~195.5°C. The mixed melting point determination with IV which was derived from III showed no depression.

Anal. Found: C, 82.25; H, 4.33. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%. I. R. max., 1250 and 1170 cm^{-1}. The I. R. spectra of these two specimens were found as superimposable over the entire region of wave length.

2-(*o*-Hydroxyphenylethynyl)-benzofurane (V).—Heating of III (1.2 g.) in 60 cc. of very diluted ethanolic sodium ethoxide for 1.5 hr. on a boiling water bath resulted in crystallization. Recrystallization from benzene yielded 0.4 g. (33%) of IV, m. p. 194.5~195.5°C. The mother liquor of the recrystallization was concentrated to form crude crystals, which were recrystallized from light petroleum (b. p. 55~75°C) employing active charcoal to give 0.5 g. (41%) of V as colorless needles, m. p. 102.5°C.

Anal. Found: C, 82.24; H, 4.33. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

U. V. max., 250, 298, 318 and 340 mμ (log ε = 3.83, 4.38, 4.44 and 4.45). I. R. max., 3380, 2207 and 1269 cm^{-1}.

V is slightly soluble in aqueous sodium hydroxide. Reaction of V with benzoyl chloride gave monobenzoate, colorless needles, m. p. 117°C.

Anal. Found: C, 81.62; H, 4.27. Calcd. for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17%.

The solution of V (0.1 g.) in ethanolic sodium ethoxide was refluxed for 3 hr., forming colorless crystals in quantitative yield. This was identified as IV by mixed melting point determination with previously obtained IV.

Ring Cleavage of 2, 2'-Dibenzofuranyl (IV).—A mixture of IV (0.4 g.), pyridine (4.0 g.) and sodium (0.3 g.) was refluxed for 3.5 hr. under nitrogen atomosphere. Water was added cautiously to the reaction mixture to decompose the unreacted sodium, and the mixture was extracted with ether. The aqueous layer was acidified with 2 N hydrochloric acid, and extracted with ether. The ethereal extract was washed with 2 N hydrochloric acid and water successively. The dried ether solution was evaporated, and the residue was repeatedly recrystallized from carbon tetrachloride affording a small amount of

* Melting points were not corrected. All U. V. and I. R. spectra were measured employing ethanolic solution and nujol mull respectively.

crystals, m. p. 140~141°C. The mixed melting point of this substance with III showed no depression.

Hunsdiecker Reaction of Silver Coumarilate (VIII). — Bromine (7.5 g.) in dry carbon tetrachloride (20 cc.) was added in one portion on well dried VIII (10.0 g.) at room temperature. Vigorous evolution of gas was observed, and the color of bromine disappeared during the period of 2 hr. The mixture was kept for 3 hr. to complete the reaction. The reaction mixture was extracted with ether, and the extract was washed with aqueous solution of sodium hydrogen carbonate to remove acidic materials. The alkaline solution was neutralized with 2 N hydrochloric acid, and extracted with ether. The ether solution was washed with water and dried. The solvent was removed by distillation and the recrystallization of the residue from aqueous ethanol gave 5 g. (56%) of 5-bromocoumarilic acid (IX), m. p. 256°C as colorless needles. (lit. value m. p. 253°C)[7].

Anal. Found: Br, 33.40. Calcd. for $C_9H_5O_3Br$: Br, 33.19%.

The ether layer which was washed with sodium hydrogen carbonate solution was washed with water and dried. The crude neutral crystals obtained by the evaporation of the solvent were recrystallized from aqueous ethanol yielding 2.0 g. (15%) of colorless needles, m. p. 81~83.5°C.

Anal. Found: Br, 67.07. Calcd. for $C_9H_3OBr_3$: Br, 67.60%.

This would be identical with so-called 2,3,7(?)-tribromocoumarone (X, m. p. 84~85°C) prepared by Stoermer[7,8].

Grateful acknowledgments for supplying coumalin are made to Shiono Perfume Industry Co., Osaka. The authors also wish to express their appreciation to Messrs. T. Shiba and M. Okumiya and Miss K. Koike for performing the elementary analyses.

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The Formation Constants of Metal Acetate Complexes. I. Polarographic Determination of the Formation Constants of Acetatonickel(II) Complexes

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In the course of our studies on the inorganic reactions involving metal complexes[1,2], the necessity for the use of the formation constants of various acetato complexes has been realized. Although many of those constants have been reported[3], they were not determined under the conditions which satisfy our present requirements. They were obtained by various researchers by various methods under various conditions.

In order to determine the formation constants of various acetato complexes under the given conditions, a systematic study has been carried out. The careful considerations of various methods which can be applied to the determination of the formation constants led to the conclusion that none of the methods is satisfactory for the present purpose. The potentiometric methods, which are considered to have the widest applicability, generally include uncertainties due to the estimation of the liquid junction potential and that of the activity coefficients of the ions present. The solubility studies have only a limited applicability. The polarographic method which was applied by Hume and his co-workers[4,5] to their study on the acetatolead(II) complexes is available only when the electrode processes are reversible at the dropping mercury electrode.

In the present paper, the principle of a new method for the determination of the

1) N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).
2) Unpublished
3) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants. Part I. Organic Ligands", The Chemical Society, London (1957), p. 3.
4) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
5) E. A. Burns and D. N. Hume, ibid., **78**, 3958 (1956).

formation constants and the application of the method to acetatonickel(II) complexes are presented. The method is similar to that proposed by Schwarzenbach and his co-workers[6-8], but applicable without data of the dissociation and the formation constants concerning the auxiliary complex-forming substance, which Schwarzenbach's method requires.

Theoretical

Let us consider the acetate buffer solution which contains nickel(II) and nitrilotriacetate (NTA) ions[9]. There exist the following equilibria:

$$Ni^{2+} + n\,OAc^- \rightleftarrows Ni(OAc)_n^{(2-n)+} \quad (1)$$

$$Ni^{2+} + X^{3-} \rightleftarrows NiX^- \quad (2)$$

$$NiX^- + H^+ \rightleftarrows NiHX \quad (3)$$

where X^{3-} denotes a tervalent NTA anion. The total concentration of nickel, $\sum[Ni]$, and that of NTA, $\sum[NTA]$, in the solution are given in terms of the ionic and molecular species as follows:

$$\sum[Ni] = [Ni^{2+}] + \sum_1^n [Ni(OAc)_n^{(2-n)+}] + [NiX^-] + [NiHX] \quad (4)$$

$$\sum[NTA] = [NTA]_f + [NiX^-] + [NiHX] \quad (5)$$

where $[Ni^{2+}]$ represents the concentration of hydrated nickel ions and $[NTA]_f$, the sum of the concentrations of uncomplexed NTA. In the polarographic measurement it is impossible to measure separately either the concentration of hydrated nickel ions or that of acetatonickel(II) complexes in an acetate medium. On the contrary, the polarographic diffusion current of nickel corresponds to the sum of the diffusion current due to the hydrated nickel ions and that due to the acetatonickel(II) complexes. If the hydrated nickel ion and the acetatonickel(II) complexes have nearly the same diffusion current constants, the sum of their concentrations can be determined from the polarographic diffusion current, if necessary, after correction.

Then, we write the equation as,

$$[Ni^{2+}]_{app.} = [Ni^{2+}] + \sum_1^n [Ni(OAc)_n^{(2-n)+}] \quad (6)$$

where $[Ni^{2+}]_{app.}$ is the concentration that can be determined from the polarographic diffusion current. Eq. 4 is rewritten as,

$$\sum[Ni] = [Ni^{2+}]_{app.} + [NiX^-] + [NiHX] \quad (7)$$

The concentrations of NiX^-, Ni^{2+} and X^{3-} are given by

$$[NiX^-] = (\sum[Ni] - [Ni^{2+}]_{app.})/\beta \quad (8)$$

$$[Ni^{2+}] = [Ni^{2+}]_{app.}/(1 + \sum_1^n K_{Ni(OAc)_n}[OAc^-]^n) \quad (9)$$

$$[X^{3-}] = [NTA]_f/\alpha \quad (10)$$

$$\alpha = 1 + \frac{[H^+]}{K_{HX}} + \frac{[H^+]^2}{K_{H_2X}K_{HX}} + \frac{[H^+]^3}{K_{H_3X}K_{H_2X}K_{HX}}$$

and $$\beta = 1 + K^H_{NiHX}[H^+]$$

where K_{H_3X}, K_{H_2X} and K_{HX} represent the first, the second and the third dissociation constant of nitrilotriacetic acid, respectively, and $K_{Ni(OAc)_n}$ and K^H_{NiHX} represent the overall formation constant of $Ni(OAc)_n^{(2-n)+}$ and the equilibrium constant of the reaction given by Eq. 3, respectively. The formation constant of NiX^-, consequently, is given as

$$K_{NiX} = \frac{[NiX^-]}{[Ni^{2+}][X^{3-}]} = \frac{\alpha\{\sum[Ni] - [Ni^{2+}]_{app.}\}\{1 + \sum_1^n K_{Ni(OAc)_n}[OAc^-]^n\}}{\beta[Ni^{2+}]_{app.}[NTA]^f} \quad (11)$$

From Eqs. 5 and 7, the concentration of uncomplexed NTA is given as,

$$[NTA]_f = [Ni^{2+}]_{app.} - \sum[Ni] + \sum[NTA] \quad (12)$$

Introducing Eq. 12 into Eq. 11, the relation

$$\frac{\{[Ni^{2+}]_{app.} - \sum[Ni] + \sum[NTA]\}[Ni^{2+}]_{app.}}{\sum[Ni] - [Ni^{2+}]_{app.}} = \frac{\alpha}{\beta K_{NiX}} + \frac{\alpha}{\beta K_{NiX}} \sum_1^n K_{Ni(OAc)_n}[OAc^-]^n \quad (13)$$

is obtained.

When the values of K_{H_3X}, K_{H_2X}, K_{HX}, K_{NiX} and K^H_{NiHX} are known, the formation constants of acetatonickel(II) complexes can be determined with Eq. 13 from the measurements of $[Ni^{2+}]_{app.}$ at n different concentrations of acetate. However, the equilibrium constant K^H_{NiHX} has not been reported and the other constants K_{H_3X},

6) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1492 (1951).
7) G. Schwarzenbach and E. Freitag, ibid., **34**, 1503 (1951).
8) H. Ackermann and G. Schwarzenbach, ibid., **32**, 1543 (1949).
9) Nickel(II) and nitrilotriacetate may be replaced by other metal ions and complex-forming substances.

K_{H_2X}, K_{HX} and K_{NiX} have been determined[6,10,11] in conditions not convenient for our study.

An alternative and better procedure for determining the formation constants of acetatonickel(II) complexes was developed. It is obvious that both α and β in Eq. 13 are constant in the solution of the given pH and the given ionic strength. The values of $[Ni^{2+}]_{app.}$ are determined by the polarographic method at the given pH and ionic strength, but at varied concentrations of acetate. The left-hand side of Eq. 13 is calculated and plotted against the concentration of acetate. If the left-hand side of Eq. 13 is denoted with F_0, it is expressed as,

$$F_0 = \frac{\alpha}{\beta K_{NiX}} + \frac{\alpha}{\beta K_{NiX}} K_{NiOAc}[OAc^-] + \frac{\alpha}{\beta K_{NiX}} K_{Ni(OAc)_2}[OAc^-]^2 + \cdots\cdots \quad (13')$$

From extrapolation of the plot to zero acetate concentration, $\alpha/\beta K_{NiX}$ is obtained. Then we obtain,

$$F_1 = \frac{F_0 - \frac{\alpha}{\beta K_{NiX}}}{\frac{\alpha}{\beta K_{NiX}}[OAc^-]} = K_{NiOAc} + K_{Ni(OAc)_2}[OAc^-] + \cdots\cdots \quad (14)$$

$$F_2 = \frac{F_1 - K_{NiOAc}}{[OAc^-]} = K_{Ni(OAc)_2} + K_{Ni(OAc)_3}[OAc^-] + \cdots\cdots \quad (15)$$

F_1 is plotted against $[OAc^-]$ and the K_{NiOAc} is determined by extrapolating the plot to zero acetate concentration. The further treatment leads to the determinations of $K_{Ni(OAc)_n}$, if higher acetato complexes are present in the solution.

Experimental

Reagents. — The solution of disodium nitrilotriacetate was prepared from the commercial nitrilotriacetic acid (DOTITE NTA), and standardized against the standard solution of copper(II) nitrate by amperometric titration with the same procedure for ethylenediaminetetraacetate[12,13]. The standard solution of nickel nitrate was prepared by dissolving a known amount of pure nickel metal in reagent-grade nitric acid. Commercial guaranteed reagents were used for buffers and supporting electrolytes without further purification.

Apparatus and Procedure. — A Shimadzu RP-2 pen-recording polarograph was used for the measurement of the current-voltage curves. The dropping mercury electrode used had an m value of 1.27 mg./sec. and a drop time t of 3.69 sec. in an air-free 0.1 M potassium chloride solution at 25°C with open circuit.

The sum of the diffusion currents of hydrated nickel ions and acetatonickel(II) complexes were determined in the acetate buffer of pH 3.83±0.01 containing nickel(II) and a slight excess of NTA at 15, 25 and 35°C. The concentration of acetate in the acetate buffer was varied from 0.05 M to 0.20 M. The ionic strength of the solution was adjusted to be 0.2 with potassium nitrate, unless otherwise stated. Polyoxyethylene lauryl ether (LEO) was added as a maximum suppressor by 1×10^{-6} M (at 15°C) or 2×10^{-6} M (at 25° and 35°C) in concentration. The pH of the solution was measured accurately, after the polarographic measurement, with a Hitachi Model EHP-1 pH meter with a glass electrode.

In the preliminary experiment, it was observed that the formation of nickel-NTA complexes nearly completed within 30 minutes under the experimental condition. Therefore, all reaction mixtures were kept in a thermostat for 3 hours to reach the completely equilibrated condition before being subjected to the polarographic measurement.

Results

The polarograms were recorded with the solutions of the same pH containing 1.00×10^{-3} M nickel nitrate, 1.12×10^{-3} M

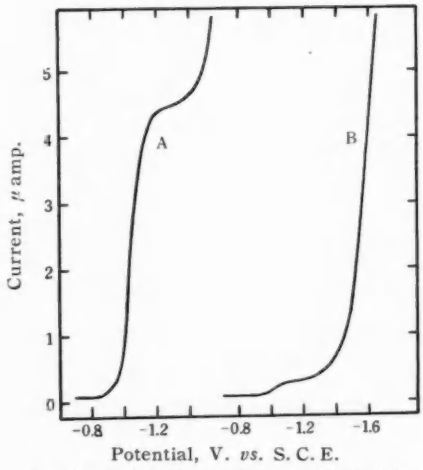

Fig. 1. Polarograms of 1.00×10^{-3} M nickel (II) obtained in the acetate-nitrate media of pH 3.83 at 25°C in the absence (curve A) and in the presence of 1.12×10^{-3} M NTA (curve B). The residual current is not corrected.

10) G. Schwarzenbach, H. Ackermann and H. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).
11) V. L. Hughes and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1319 (1956).
12) N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst (Bunseki Kagaku)*, **6**, 86 (1957).
13) N. Tanaka, I. T. Oiwa and M. Kodama, *Anal. Chem.*, **28**, 1555 (1956).

NTA and various concentrations of acetate. Fig. 1 shows the polarograms obtained in the absence and the presence of a slight excess of NTA. Nickel(II) gives an irreversible wave with the half-wave potential of about −1.05 volts *vs.* S. C. E. in the acetate-nitrate media. (Curve A in Fig. 1). This wave is due to the reductions of the hydrated nickel(II) ions and the acetatonickel(II) complexes. The presence of a slight excess of NTA decreases to a great extent the height of the nickel wave, but does not obliterate the wave completely. A small wave which was followed by the depolarization of the supporting electrolyte is clearly seen in Fig. 1 (Curve B). The limiting current of the wave was found to be proportional to the square root of the effective height of mercury column on the dropping mercury electrode. This clearly showed that the limiting current is diffusion-controlled and is proportional to the concentration of the electroactive species.

The apparent diffusion current constants were determined from the measurement of the diffusion current of nickel(II) at various acetate concentrations at the given ionic strength. In Fig. 2, typical examples

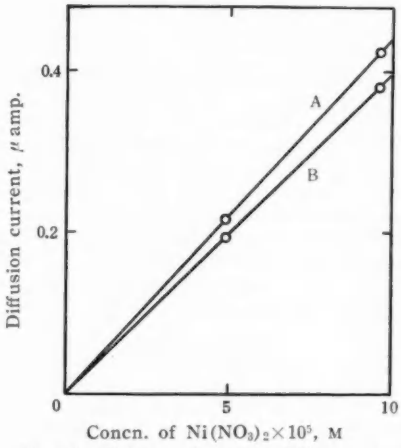

Fig. 2. Relation between diffusion current and concentration of nickel nitrate in acetate buffer solutions of pH 3.83 at 25°C. Acetate concentrations are: A, 0.05 M; B, 0.20 M.

of those measurements are given. The values of $[Ni^{2+}]_{app.}$ of Eq. 6 were calculated with the aid of those diffusion current constants from the limiting currents obtained with reaction mixtures. The results are given in Table I, which indicate that $[Ni^{2+}]_{app.}$ increases with increasing concentration of acetate.

The left-hand side of Eq. 13 was calculated with the values of $[Ni^{2+}]_{app.}$ given in Table I, and was plotted against the acetate concentration. The results are

TABLE I. $[Ni^{2+}]_{app.}$ OBTAINED EXPERIMENTALLY AT VARIOUS TEMPERATURES

Concn. of acetate, M	$[Ni^{2+}]_{app.} \times 10^5$, M		
	15°C	25°C	35°C
0.05	3.77	3.86	3.87
	3.80	3.77	3.89
0.10	4.06	4.11	4.23
	4.12	4.19	4.30
			4.30
0.15	4.46	4.42	4.63
	4.33	4.50	4.54
			4.63
0.20	4.78	4.76	4.87
	4.66	4.88	4.83
			4.87

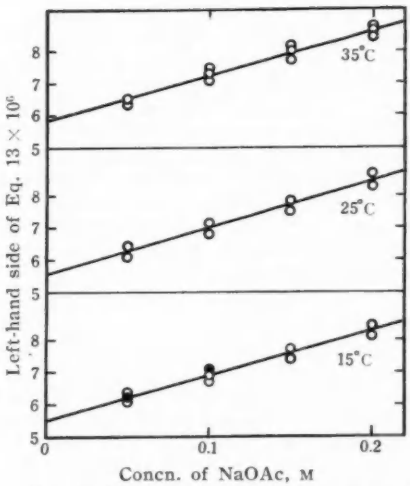

Fig. 3. Relation between the value of left-hand side of Eq. 13 and the concentration of acetate at various temperatures. ○ indicates the values obtained in nitrate media, and ● in perchlorate media.

shown in Fig. 3, where it is clearly seen that there is a linear relation between the values of the left-hand side of Eq. 13 and the concentration of acetate. This indicates conclusively that only one type of acetato complex, $NiOAc^+$, exists in the solution under the experimental condition. From the plots in Fig. 3, the values of

$\alpha/\beta K_{NiX}$ and $\alpha K_{NiOAc}/\beta K_{NiX}$ in Eq. 13' were determined, the former being given by the intersept at $[OAc^-]=0$ and the latter, by the slope. The experimental results obtained at 25°C were also treated by the least square method, with the result that the probable errors of $\alpha/\beta K_{NiX}$ and $\alpha K_{NiOAc}/\beta K_{NiX}$ were ±1.5% and ±4.1%, respectively. The formation constants of the monoacetatonickel(II) complex at 15°, 25° and 35°C were obtained by dividing the values of $\alpha K_{NiOAc}/\beta K_{NiX}$ by those of $\alpha/\beta K_{NiX}$. These are given in Table II.

TABLE II. FORMATION CONSTANTS OF MONOACETATONICKEL(II) COMPLEX AT VARIOUS TEMPERATURES

Temp., °C	K_{NiOAc}
15	2.6
25	2.6
35	2.4

Discussions

The formation constants of monoacetatonickel(II) complex, K_{NiOAc}, are found to be almost independent of temperature in the range from 15° to 35°C. Jena, Aditya and Prasad[14] studied the acetatonickel(II) complex by the e.m.f. method and reported the thermodynamic formation constant of the monoacetatonickel(II) complex to be 13.5 at 30°C. The formation constant at ionic strength 0.2 was calculated from this value to be 4.5, when the activity coefficient of acetate ions was assumed to be equal to that of monoacetatonickel(II) ions and the activity coefficient of nickel ions was estimated to be 0.33[15]. The resulting value of 4.5 seemed to be in good agreement with the formation constant obtained in this study. Both values were determined by completely different methods and the value obtained by the e. m. f. method involves the uncertainty due to the estimation of the activity coefficient. Fronaeus[16] studied the formation of the complex by means of the ion-exchanger and also by means of the measurement with a quinhydrone electrode and obtained the formation constants of 4.7 and 5.5, respectively, at ionic strength 1.0 (sodium perchlorate) at 20°C. They also seem to support the value obtained in this study.

The experimental solution contained a certain quantity of potassium nitrate, which was added to adjust the ionic strength of the solution. It is expected that the nitrate ion has such a small tendency to form a complex with the nickel(II) ion that it seems unnecessary to consider the effect of the nitrate ion in the present calculation. The confirmation of this was attained in the comparison of the experimental results observed in nitrate and perchlorate media. The perchlorate has been known to have the least complex-forming ability. If an appreciable amount of nitrato complex is formed in the nitrate media, the values of the left-hand side of Eq. 13 obtained at the same concentration of acetate are expected to be larger in the nitrate media than in the perchlorate media. The measurement of $[Ni^{2+}]_{app.}$ was carried out in the solution of which the ionic strength was adjusted with sodium perchlorate instead of potassium nitrate. The value of $[Ni^{2+}]_{app.}$ agreed completely with that obtained in the solution containing nitrate. From this fact it may be concluded that the nitrate ions show least complex-forming tendency and, consequently, the use of nitrate ions requires no correction on the present calculation.

In conclusion it should be noted here that the method for the determination of the formation constant given in this paper may be applicable to the study of other metal complexes of relatively small formation constants. The method is more rigorous than the e. m. f. method, because the latter method requires the estimations of the liquid junction potential and the activity coefficient. The determination of the sum of the concentration of hydrated nickel ions and that of acetatonickel(II) complexes may be carried out by other methods.

Summary

A new method for the determination of the formation constants of metal acetate complexes has been developed. The method is based on the polarographic measurement of the sum of the equilibrium concentrations of hydrated metal ions and metal acetate complexes in the presence of an appropriate auxiliary complex-forming substance. One of the advantages of the method is that no estimation is required in the course of the calculation. The other is that no information of the dissociation and formation constants is

14) P. K. Jena, S. Aditya and B. Prasad, *J. Indian Chem. Soc.*, **30**, 735 (1953).
15) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).
16) S. Fronaeus, *Acta Chem. Scand.*, **6**, 1200 (1952).

required concerning the auxiliary complex-forming substance.

The method is applied to the study of acetatonickel(II) complexes using nitrilotriacetate as an auxiliary ccmplex-forming substance. The results reveal that only monoacetatonickel(II) ions, $NiOAc^+$, exist in the solution containing acetate up to 0.2 M in concentration. The formation constants K_{NiOAc} at ionic strength 0.2 are calculated to be 2.6 at 15°C, 2.6 at 25°C and 2.4 at 35°C.

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Effects of Protonation on the Electronic Structure and Spectra of Nitrogen Heterocycles

By Shizuyo MATAGA and Noboru MATAGA

(Received October 21, 1958)

In the previous papers[1-3], we have reported detailed theoretical studies about the protonation effects on the electronic spectra of some nitrogen heterocycles. In these reports, the interaction between proton and a nitrogen heterocycle has been treated by various approximations. Among these, the following two are most representative.

i) It has been assumed that there is no transfer of non-bonding electrons on nitrogen toward proton but bare proton is located near the nitrogen atom of neutral molecule. Thus, the electrostatic potential due to proton has been added to the core potential in the total π-electronic Hamiltonian and nuclear attraction integrals which arise owing to this potential have been computed theoretically employing the usual Slater $2p\pi$ AO's.

ii) It has been considered that there is a strong charge transfer from nitrogen atom to proton leading to covalent binding between them and molecular integrals have been evaluated semi-empirically using valence-state ionization potential and electron affinity of N^+ atom.

By means of the semi-empirical Hartree-Fock SCF MO's obtained with these integrals, the electronic spectra of protonated nitrogen heterocycles have been calculated. The calculated spectra by the method i have been in very good agreement with those experimentally obtained. However, the calculation with the method ii has led to a result which is in rather poor agreement with the experimental values. A careful examination of these results has led to the following conclusion. In the case of the later method, the inductive charge displacement in σ-core caused by the charge transfer of non-bonding electrons from nitrogen atom toward proton may not be appropriately accounted, where the core potential is very deep at nitrogen and the same as that in the neutral molecule, at the carbon atoms. In the case of the method i), however, the displacement in σ-core may be appropriately taken into consideration by the formal use of the electrostatic proton potential, which may be the cause of the superiority of this method.

If the unsatisfactory results obtained with the method ii originates from the neglect of the inductive charge displacement in σ-core caused by protonation as described above, one may be able to improve the results by taking into consideration the inductive displacement in σ-core in some appropriate manner. In this respect, we have calculated the electronic structures and spectra of pyridinium ion and pyrazinium diion employing

1) N. Mataga and S. Tsuno, *Naturwiss.*, **45**, 333 (1958).
2) S. Mataga and N. Mataga, *Z. Physik. Chem. N. F.*, in press.
3) S. Mataga and N. Mataga, This Bulletin, **32**, 511 (1959).

the self-consistent electronegativity method proposed by Brown and Heffernan[4] which may be regarded as an improvement of the method ii. Our calculation procedure is essentially the same as that of Brown and Heffernan but a little different from theirs in some details of actual compution procedures. In the present paper, we shall report the results of this calculation with some discussions. In addition, results of some critical studies about the effects of protonation on the core energies and diagonal elements of Fock's Hamiltonian, $F_{\mu\mu}$'s, will be given comparing the present results with previous ones.

Application of Self-Consistent Electronegativity (SCE) Method

In SCE method, it is assumed that Slater's rules for effective charges of atoms are applicable for continuous variation in electron density. Accordingly, for atoms in the first row of the periodic table the relationship is

$$Z_\mu = N_\mu - 1.35 - 0.35\ (\sigma_\mu + P_{\mu\mu}) \qquad (1)$$

where N_μ is the atomic number of μ atom and σ_μ is the number of σ-electrons associated with μ atom in the molecular framework, e.g. 3 for carbon and positively charged nitrogen in pyridinium ion. $P_{\mu\mu}$ is the π-electron density on μ atom. If this variation of Z_μ with $P_{\mu\mu}$ is included in the SCF MO procedure, in addition to the usual functional dependence of the SCF matrix elements upon the charge distribution, the various molecular integrals become functions of $P_{\mu\mu}$ from their dependence on Z_μ. The methods of allowing for this variation are as follows.

Firstly, the form of the relationship between the valence state ionization potential I_μ and Z_μ should be established.

Various valence-state ionization potentials have been calculated from the experimental term values of atomic spectra. If I_μ's are plotted against Z_μ's for the (sp^3, V_4) valence state of the iso-electronic series, C, N^+, O^{2+} and for the (sp^4, V_3) valence state of the iso-electronic series, C^-, N, O^+, respectively, the curves are accurately parabolic:

$$I_\mu(sp^3, V_4) = 3.490\, Z_\mu^2 - 8.541\, Z_\mu + 2.446 \qquad (2)$$

$$I_\mu(sp^4, V_3) = A_\mu(sp^3, V_4) = 3.730\, Z_\mu^2 - 16.285\, Z_\mu + 14.108 \qquad (3)$$

where A_μ is the valence state electron affinity. These equations are used for evaluating I_{C^-} and I_{N^+}. Then, from these eqs., the mono-centric inter-electronic coulomb repulsion integral, $\gamma_{\mu\mu}$, is easily obtained as,

$$\gamma_{\mu\mu}(sp^3, V_4) = I_\mu(sp^3, V_4) - A_\mu(sp^3, V_4) = -0.240\, Z_\mu^2 + 7.743\, Z_\mu - 11.662 \qquad (4)$$

The two-center electronic coulomb repulsion integral, $\gamma_{\mu\nu}$, was evaluated as in our previous works[2,5-7] from the formula,

$$\gamma_{\mu\nu} = e^2/(a_{\mu\nu} + r_{\mu\nu}) \qquad (5)$$

where parameter $a_{\mu\nu}$ has been determined by the equations:

$$a_{\mu\nu} = 2a_{\mu\mu}\cdot a_{\nu\nu}/(a_{\mu\mu} + a_{\nu\nu}) \qquad (6)$$

$$a_{\mu\mu} = 14.3949/\gamma_{\mu\mu} \qquad (7)$$

The other quantities necessary for the calculation are the values of off-diagonal matrix elements of core Hamiltonian, $\beta_{\mu\nu}$. We have used the same values as before[2] for these quantities.

With the parameters described above, SCE LCAO MO's of pyridinium ion and pyrazinium diion have been obtained by the iterative process in which all integrals except $\beta_{\mu\nu}$ depend on the π-electron distribution.

The results are collected in Table I and

TABLE I. SCE MO's AND MO ENERGIES OF PYRIDINIUM ION AND PYRAZINIUM DIION

Pyridinium ion

Symmetry	ε_i(eV.)	
b_2	−18.3382	$\phi_1 = 0.1200(\phi_2+\phi_6) + 0.3272(\phi_3+\phi_5) + 0.0763\,\phi_1 + 0.8667\,\phi_4$
b_2	−13.1857	$\phi_2 = 0.4791(\phi_2+\phi_6) + 0.1121(\phi_3+\phi_5) + 0.6631\,\phi_1 - 0.2758\,\phi_4$
a_2	−11.4409	$\phi_3 = 0.4939(\phi_2-\phi_6) + 0.5059(\phi_3-\phi_5)$
b_2	− 3.3504	$\phi_4 = 0.1846(\phi_2+\phi_6) + 0.4811(\phi_3+\phi_5) - 0.5805\,\phi_1 - 0.3632\,\phi_4$
a_2	− 1.8341	$\phi_5 = 0.5059(\phi_2-\phi_6) - 0.4939(\phi_3-\phi_5)$
b_2	0.6149	$\phi_6 = 0.4711(\phi_2+\phi_6) - 0.3859(\phi_3+\phi_5) - 0.4663\,\phi_1 + 0.2020\,\phi_4$

Pyrazinium diion

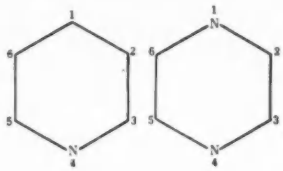
b_{2u}	−19.7914	$\phi_1 = 0.2637(\phi_2+\phi_3+\phi_5+\phi_6) + 0.6007(\phi_1+\phi_4)$
b_{4g}	−18.6618	$\phi_2 = 0.1781(\phi_2-\phi_3-\phi_5+\phi_6) + 0.6607(\phi_1-\phi_4)$
b_{1g}	−12.1179	$\phi_3 = 0.5000(\phi_2+\phi_3-\phi_5-\phi_6)$
b_{2u}	− 5.3902	$\phi_4 = 0.4248(\phi_2+\phi_3+\phi_5+\phi_6) - 0.3729(\phi_1+\phi_4)$
a_{1u}	− 2.6605	$\phi_5 = 0.5000(\phi_2-\phi_3+\phi_5-\phi_6)$
b_{3g}	− 0.7302	$\phi_6 = 0.4672(\phi_2-\phi_3-\phi_5+\phi_6) - 0.2518(\phi_1-\phi_4)$

4) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

5) N. Mataga and K. Nishimoto, *Z. Physik. Chem. N. F.*, **13**, 140 (1957).

6) N. Mataga, This Bulletin, **31**, 453, 459, 463 (1958).

7) N. Mataga, *Z. Physik. Chem. N. F.*, **18**, 19 (1958).



(I) (II)

Fig. 1. Numbering of atoms in pyridine (I) and pyrazine (II).

the numbering of atoms is indicated in Fig. 1.

The spectra of these ions calculated with these MO's are given in Table II in comparison with the observed values.

TABLE II. CALCULATED AND OBSERVED SPECTRA OF PYRIDINIUM ION AND PYRAZINIUM DIION

Symmetry	Pyridinium ion Excitation energy Calcd.	Obsd.	Calcd. Oscillator strength**
$^1B_1(^1L_b)$	4.7492	4.83	0.346
$^1A_1(^1L_a)$	6.1375	5.50	0.000
$^1A_1(^1B_a)$	7.1336	—	1.108
$^1B_1(^1B_b)$	7.7588	—	0.535

* V. Zanker, *Z. Physik. Chem. N. F.*, **2**, 52 (1954).

** The observed oscillator strengths of pyridinium ion are uncertain. Although ^1L_b band of pyridine is intensified by protonation, the oscillator strength of ^1L_b band may be almost equal to that of ^1L_a band in its order of magnitude, in the case of pyridinium ion.

Symmetry	Pyrazinium diion Excitation energy Calcd.	Obsd.*	Calcd. Oscillator strength**
$^1B_{3u}(^1L_b)$	4.1412	4.35	0.641
$^1B_{1u}(^1L_a)$	6.5108	(6≲)	0.472
$^1B_{1u}(^1B_a)$	9.5635	—	0.454
$^1B_{3u}(^1B_b)$	11.5009	—	0.624

* F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 712 (1951) and S. Mataga, unpublished.

** The observed oscillator strength of pyrazinium diion is uncertain. The oscillator strength of ^1L_b band, however, seems to be two or three times as large as that of a neutral molecule. (The calculated oscillator strength of ^1L_b band in the case of pyrazine molecule is 0.162[5]).

The agreement of the calculated spectra with observed values as given in Table II, is not satisfactory. There is not such nice agreement with experiment as seen in the previous calculation[1-3] with method i as described in the introductory part of this paper, and the present result seems to be only a small improvement of the previous calculation[1-3] with the method ii. Accordingly, the present unsatisfactory results may originate from the same circumstance as in the case of the previous calculation with the method ii, i.e., from the insufficient consideration of the inductive charge displacement in the σ-core caused by the transfer of nonbonding electrons on nitrogen atom toward proton. In this respect, some critical discussions about the effects of protonation on the electronic structure of these nitrogen heterocycles will be given in the next section.

On the Inductive Charge Displacement in the σ-Core Caused by the Protonation

In the method i, the electrostatic potential due to proton is simply added to the core Hamiltonian and the diagonal element of Fock's Hamiltonian in terms of AO's has the following form:

$$F_{\mu\mu}=\alpha_\mu+V_\mu{}^P+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu}+\sum_{\kappa(\neq\mu)}(P_{\kappa\kappa}-1)\gamma_{\mu\kappa} \quad (8)$$

where

$$\alpha_\mu=\int\phi_\mu(i)\left\{-\frac{1}{2}\Delta_i{}^2-V_\mu(i)\right\}\phi_\mu(i)\mathrm{d}v(i)=-I_\mu$$

$$V_\mu{}^P=-e^2\int\sum_P\frac{\phi_\mu{}^2(i)}{r_{Pi}}\mathrm{d}v(i)$$ and r_{Pi} is the distance between proton and i-th electron.

As pointed out before[2,3], the changes in the core energies produced by protonation may be almost completely contributed by the inductive displacement in σ-core. Then, in view of the short range character of the interactions in σ-core, the additional core energy, i.e., $V_\mu{}^P$, used in the method i may be too large. It seems probable $V_\mu{}^P=0$ at the atom in the opposite side of proton. However, if we use $(V_\mu{}^P-V_0{}^P)$'s instead of $V_\mu{}^P$'s where $V_0{}^P$ is the additional core energy at the atom in the opposite side of proton, it is evident that, in our approximation, the MO's calculated by method i stay unchanged although the MO energies are lifted by $|V_0{}^P|$ uniformly. Accordingly, one may be allowed to say that the real changes in core energies due to inductive displacement are represented by $(V_\mu{}^P-V_0{}^P)$, because the calculated spectra with method

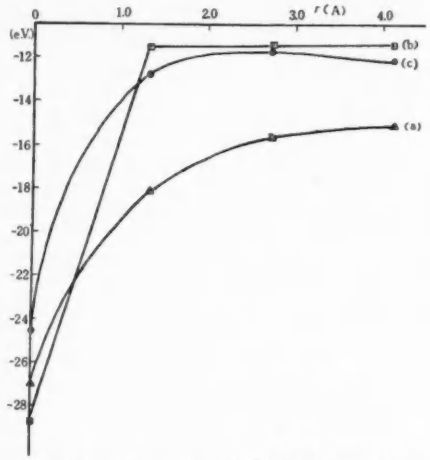


Fig. 2. α_μ's or $(\alpha_\mu + V_\mu^P)$ plotted against the distance r along the bonds between the protonated nitrogen and μ-th atom in the case of pyridine. (a) method i, (b) method ii, (c) SCE method.

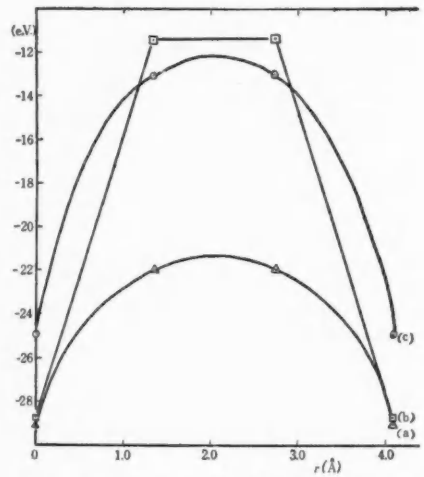


Fig. 3. α_μ's or $(\alpha_\mu + V_\mu^P)$ plotted against the distance r along the bonds in the case of pyrazine. (a) method i, (b) method ii, (c) SCE method.

i are in a very good agreement with experiment[1-3].

Now, the circumstance mentioned at the end of the last section is evident from Figs. 2 and 3 where α_μ's in the method ii and SCE method, and $(\alpha_\mu + V_\mu^P)$'s in the method i are plotted against the distance along the bonds between protonated atom and μ atom. Moreover, $F_{\mu\mu}$'s which may be regarded as a kind of effective electro-

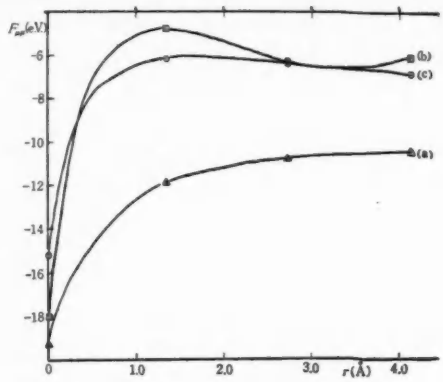


Fig. 4. $F_{\mu\mu}$'s plotted against the distance r along the bonds between the protonated nitrogen and μ-th atom in the case of pyridine. (a) method i, (b) method ii, (c) SCE method.

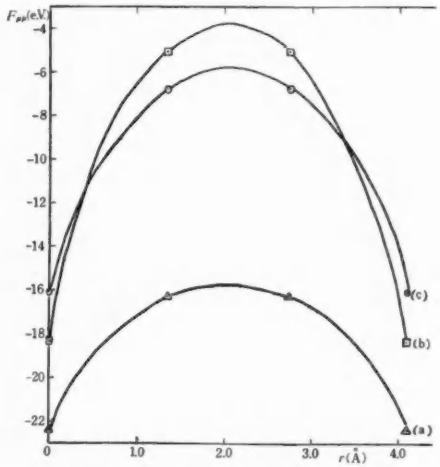


Fig. 5. $F_{\mu\mu}$'s plotted against the distance r along the bonds in the case of pyrazine. (a) method i, (b) method ii, (c) SCE method.

negativity of μ atom in the molecule[2,5] show the same tendencies as α_μ's and $(\alpha_\mu + V_\mu^P)$'s, respectively, in Figs. 4 and 5.

In these figures, the results obtained by the SCE method are rather close to the results obtained by the method ii, which may be the most predominant factor that leads to the unsatisfactory prediction of electronic spectra by the former method.

Now, in the case of protonated pyridine, if we put:

$$\alpha_\mu' - \theta = (\alpha_4' - \theta)/\nu^n \qquad (9)$$

where $\alpha_\mu' = (\alpha_\mu + V_\mu^{r})$, θ and ν are parameters to be determined semiempirically and n is the number of bonds between nitrogen and μ atom, then the values of α_μ' plotted in Fig. 2 are well reproduced by this equation putting $\theta = 14.86$ eV. and $\nu = 4$.

If we approximate the distances from nitrogen along the bonds by $r = n \cdot \lambda$ where λ is the average bond distance of pyridine, i.e., 1.38 Å, then Eq. 9 becomes

$$\alpha_\mu' - \theta = (\alpha_4' - \theta)/\nu^{r/\lambda} \qquad (10)$$

Actually, Eq. 10 is valid.

Similar equations have been obtained also for $F_{\mu\mu}$'s as follows:

$$(F_{\mu\mu} - 10.50) = (F_{44} - 10.50)/6^{n} \qquad (11)$$

$$\text{or} \quad = (F_{44} - 10.50)/6^{r/1.38} \qquad (12)$$

The value of θ in Eqs. 9 and 10 and the corresponding quantity in Eqs. 11 and 12 are very close to α_1' and F_{11}, respectively.

Therefore, these equations may be regarded as representing the inductive displacement caused by protonation and also that the inductive effect due to protonation is practically negligible on the atom which is more than two-bond distance apart from the protonated nitrogen atom.

Then, Eqs. 9 and 10 may be useful in general for the study of the protonation effect on the electronic structure of nitrogen heterocycles, although the behaviour of $F_{\mu\mu}$ may be characteristic of each molecule and Eqs. 11 and 12 can not be used in general. It is customary in the simple MO theory to take into consideration the inductive effect assuming the form of coulomb integral as $\alpha_\mu = \alpha + \delta_\mu \beta$ It has been pointed out[2] that the SCF MO's and charge distributions calculated by the method i are well reproduced with simple MO's obtained using the values of coulomb integrals $\alpha_4 = \alpha + 2.4\,\beta$, $\alpha_3 = \alpha_5 = \alpha + 0.4\,\beta$ and assuming the all resonance integrals are equal to β. Then $\delta_3 = \delta_5 = \delta_4/6$, which is the same relationship as in the case of $F_{\mu\mu}$, i.e., by Eq. 11 $\Delta F_{33} = \Delta F_{55} = \Delta F_{44}/6$, where $\Delta F_{\mu\mu} = (F_{\mu\mu} - 10.50)$

Although, in the case of the protonated pyrazine, we can not obtain the relationship as Eqs. 9—12, because of the higher symmetry of the molecule, the circumstance may be analogous to the case of protonated pyridine.

Summary

The self-consistent electronegativity method has been applied to calculate the electronic structure and spectra of some protonated nitrogen heterocycles. This method may be regarded as an improvement of our method ii which has led to poor agreement with experiment because of the neglect of the inductive displacement in σ-core caused by protonation. The calculated results with the present method, however, are in rather poor agreement with experiment, and it is only a small improvement of the method ii.

Comparing the present results with the previous ones obtained with method i and ii, some discussions about the nature of the protonation effect on the electronic structure of these molecules have been given. In addition, formulae which represent the magnitude of inductive effect on each atom as a function of the distance or number of bonds from the protonated atom have been given.

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SHORT COMMUNICATIONS

Photochemical Decomposition of 2,4,6-Trinitrophenyl Amino Acids and Peptides

By Kazuo SATAKE and Tsuneo OKUYAMA

(Received February 9, 1959)

The unstability of dinitrophenyl amino acids to sunlight was already described by Sanger[1], Mills[2], and Blackburn[3]. Akabori et al.[4] also studied the rate of the photochemical decomposition of various dinitrophenyl amino acids by exposure to a tungsten lamp.

Trinitrophenyl (TNP) amino acids and peptides, synthesis of which is going to be published elsewhere, have similar properties to dinitrophenyl derivatives and are also labile photochemically.

A saturated solution of TNP-amino acid in 1 N hydrochloric acid was prepared 20 ml. of the solution was placed in a petri dish (8 cm. in diameter) and exposed to ultraviolet light (Mazda UV-sterilizing lamp)or sunlight. The absorption spectrum of the solution changed gradually to that of picramide. It suggests the formation of picramide by the photochemical decomposition of TNP-amino acids. When the solution showed the absorption spectrum of picramide, it was concentrated to dryness under reduced pressure. The residue was dissolved in a small amount of ethanol and applied to filter paper. The presence of picramide and the absence of free amino acids were verified by means of one-dimensional paper chromatography on Toyo No. 51 filter paper. The solvent systems used were phenol-water (4 : 1, v/v), 1.5 M phosphate buffer (pH 5.6) or butanol saturated with 2 N ammonia.

By further exposure to light (after 24 ~44 hr.), no ninhydrin positive substance was detected by two-dimensional paper chromatography of the concentrated samples, although the decoloration of the solution was observed, indicating the complete decomposition of the TNP-amino acid. A yellow substance, probably resulting from picramide, was then precipitated. Conditions of the two-dimensional paper chromatography were as follows: ascending method, on Toyo No. 51 filter

TABLE I. PHOTODECOMPOSITION OF TNP-AMINO ACIDS AND -PEPTIDES

TNP-compound	Solvent	Photodecomposition products: Ninhydrin positive substance	Recovery of amino acid (%)
TNP-glycine	1 N HCl	none	0
TNP-DL-alanine	1 N HCl	none	0
TNP-L-leucine	1 N HCl	none	0
TNP-L-valine	1 N HCl	none	0
〃	1 N HCl-Dioxane*	valine (?), unknown	—
〃	1 N HCl-Ethanol*	none	0
TNP-glycyl-glycine	1 N HCl	glycine	93
〃	1 N HCl-Dioxane*	glycine, glycyl-glycine, unknown	—
TNP-glycyl-leucine	1 N HCl	leucine	—
TNP-glycyl-DL-valine	1 N HCl	valine	87
TNP-glycyl-DL-serine	1 N HCl	serine	91
TNP-alanyl-DL-asparagine	1 N HCl	asparagine	83
TNP-L-leucyl-L-tyrosine	1 N HCl	tyrosine	92
TNP-glycyl-glycyl-glycine	1 N HCl	glycyl-glycine	—

* 1:1, v./v.

1) F. Sanger, *Biochem. J.*, **45**, 563 (1949).
2) G. L. Mills, ibid., **50**, 707 (1952).
3) S. Blackburn, ibid., **45**, 579 (1949).
4) S. Akabori, T. Ikenaka, Y. Okada and K. Kohno, *Proc. Japan Acad.*, **29**, 509 (1953).

paper, using butanol-acetic acid-water (4:1:1, v/v) as the first developer and phenol-water (4:1, v/v) as the second.

In the cases of TNP-peptides, the similar photochemical decomposition was observed. Only the trinitrophenylated amino-terminal amino acid residue was decomposed photochemically, while the second residue was liberated in a free state.

The liberated amino acid was estimated by the TNP-method, which was composed of the trinitrophenylation of amino acids with picryl sulfonate, followed by the colorimetry at 340 mμ[5]. The recoveries of amino acids were listed on Table I. The amino acid liberation was caused exclusively by the photochemical decomposition of the TNP-amino-terminal amino acid residue, since no amino acid was released by the similar treatment of TNP-peptide without exposure to light, or of free dipeptide with exposure to light.

In the case of TNP-triglycine, glycylglycine was liberated, but no release of glycine could be observed.

These results suggest a probable application for a new method of the stepwise degradation of peptide from the amino terminal. Detail of these studies will be the subject of the future communication.

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5) K. Satake, T. Okuyama and M. Ohashi, unpublished paper.

Ionic Character and Hybridization of Ammonia Molecule

By Yoshifumi KATO*, Utaro FURUKANE and Haruo TAKEYAMA

(Received February 9, 1959)

Townes and Dailey[1] have determined the electronic structure of molecules from the nuclear quadrupole coupling constants. In the present paper, this theory has been applied to the ammonia molecule. On the basis of the theoretical results, together with the experimental value of the dipole moment, some discussion has been made on the ionic character of the N–H bond and the *s–p* hybridization of the nitrogen atom. The following VB function has been assumed to the ground state of the molecule,

$$\Psi_T = A\,[\Psi_{cov} + 3\lambda\Psi_{ion1} + 3\lambda^2\Psi_{ion2} + \lambda^3\Psi_{ion3}] \quad (1)$$

Here A represents the normalization factor, the coefficient λ is concerned with the magnitude of the ionic character of the N–H bond and the wavefunctions Ψ_{ion1}, Ψ_{ion2}, and Ψ_{ion3} respectively refer to the singly, doubly and triply ionized structure. To each configuration the following electron pair bond functions are assumed:

$$\begin{aligned}
\Psi_{cov} &= (N_l)^2(N_1H_1)^2(N_2H_2)^2(N_3H_3)^2 \\
\Psi_{ion1} &= (N_l)^2(N_1)^2(N_2H_2)^2(N_3H_3)^2 \\
\Psi_{ion2} &= (N_l)^2(N_1)^2(N_2)^2(N_3H_3)^2 \\
\Psi_{ion3} &= (N_l)^2(N_1)^2(N_2)^2(N_3)^2
\end{aligned} \quad (2)$$

Here N_l and N_i ($i=1$, 2 and 3) are the lone pair orbital and the equivalent orbitals on the nitrogen atom and $(N_iH_i)^2$ is the normalized bond orbital of the Heitler-London type. When the structure of the ammonia molecule is considered to belong to the symmetry species C_{3v}, N_l and N_i orbitals are expressed as follows:

$$\begin{aligned}
H_l &= \alpha S + \sqrt{3}\,\beta P_z \\
N_1 &= \gamma S + \sqrt{\frac{1}{6}}\,\delta P_x + \sqrt{\frac{1}{2}}\,\delta P_y + \sqrt{\frac{1}{3}}\,\varepsilon P_z \\
N_2 &= \gamma S + \sqrt{\frac{1}{6}}\,\delta P_x - \sqrt{\frac{1}{2}}\,\delta P_y + \sqrt{\frac{1}{3}}\,\varepsilon P_z \\
N_3 &= \gamma S - \sqrt{\frac{2}{3}}\,\delta P_x + \sqrt{\frac{1}{3}}\,\varepsilon P_z
\end{aligned} \quad (3)$$

Here S, P_x, P_y and P_z represent the Slater AO's and the coordinate system was taken as shown in Fig. 1. By considering the orthonormalization conditions for Eq. 3, the number of coefficients to be determined is reduced to only one ε.

The dipole moment and the quadrupole coupling constant are expressed as follows:

$$\mu = e\Big(\sum_{i=1}^{3} r_i - \sum_{j=1}^{8} \bar{Z}_j\Big),\quad \bar{Z}_j = \int |\Psi_T|^2 Z_j \mathrm{d}v \quad (4)$$

$$eQq = -e^2Q\int |\Psi_T|^2 (3\cos^2\theta_z - 1) r^{-3}\mathrm{d}v \quad (5)$$

$$\approx eQq_{pz} f(\lambda, \varepsilon) \quad (5')$$

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1) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

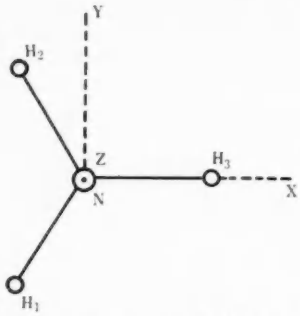

Fig. 1. The coordinate system of NH_3 molecule. Length N-H=1.014 Å. Angle H_i-N-H_j=106° 47' [11].

$$q_{pz} = -e\int|\Psi_{n:2pz}|^2(3\cos^2\theta_z - 1)r^{-3}\mathrm{d}v \qquad (6)$$

(e: protonic charge, 4.802×10^{-10} e.s.u.)

We followed the theory of Townes and Dailey that the contribution to the field gradient at the nitrogen nucleus depends exclusively upon the p electrons of the nitrogen atom. Moreover, since we have had no experimental value for eQq_{pz} of the nitrogen atom, we used a value $-11.12\,Mc.$ calculated with the aid of the $2pz$ SCF AO of the ground state ^4S of the nitrogen atom, which was obtained to fit to Hartree-Fock field by Hartree and Hartree[2]. We used the microwave data for the experimental values, $\mu=1.468\,D$ and $eQq=-4.0842\,Mc.$[3], and all the overlap integrals and the dipole moment matrix integrals were evaluated by the ordinary method[4]. These values are tabulated in Table I.

TABLE I. OVERLAP INTEGRAL: $S_{ab}=\int\chi_a\chi_b\mathrm{d}v$

DIPOLE MOMENT MATRIX INTEGRAL:

$$M_{ab}=\int\chi_a Z\chi_b\mathrm{d}v \text{ (in } a.u.).$$

The following abbreviated notations for AO's are used: h_i=(H: 1s), s=(N: 2s), x=(N: 2px), y=(N: 2py) and z=(N: 2pz).

S_{h_1s}	0.510836	$M_{h_1h_1}$	0.718747
S_{h_1z}	0.151483	M_{h_1s}	0.168502
S_{h_1x}	−0.187118	M_{h_1z}	0.461132
S_{h_2x}	−0.187118	M_{sz}	0.0866768
S_{h_3x}	0.374235	M_{h_1x}	0.0640552
		M_{h_2x}	0.0640552
		M_{h_3x}	0.128110
		M_{h_1y}	0.111230
		M_{h_2y}	0.111230
		M_{h_3y}	0

The parameters ε and λ were determined as 0.9465 and −0.38, respectively, by the aid of Eqs. 4 and 5′, and the observed values of μ and eQq. The normalized hybrid orbitals of the nitrogen atom then become,

$$\left.\begin{aligned} N_l &= 0.8395S - 0.5434P_z \\ N_1 &= 0.3137S - 0.4082P_x - 0.7071P_y \\ &\quad + 0.4847P_z \\ N_2 &= 0.3137S - 0.4082P_x + 0.7071P_y \\ &\quad + 0.4847P_z \\ N_3 &= 0.3137S + 0.8165P_x + 0.4847P_z \end{aligned}\right\} \qquad (2)$$

TABLE II. RELATIVE WEIGHTS OF VALENCE STRUCTURE IN NH_3 AND S CHARACTER OF THE HYBRID ORBITAL OF N ATOM

Structure		Weight of structure % Present	Syrkin et al.
Covalent form	(I)	14.5	16
Single ionic form	(II)	18.8	13.5
Double ionic form	(III)	2.7	3.9
Triple ionic form	(IV)	0.1	0.3
Transitional	(I)—(II)	33.0	27.3
〃	(I)—(III)	12.5	15
〃	(I)—(IV)	1.6	3
〃	(II)—(III)	14.3	15
〃	(II)—(IV)	1.8	4
〃	(III)—(IV)	0.7	2

	S character % Present	Duncan & Pople	Higuchi
For lone pair orb.	70.5	38.9	71.4
For equivalent orb. (each)	9.8	4.1	3.2

Thus we get the estimates of the ionic character and the s–p hybridization of NH_3 molecule. These are given in Table II, together with the estimated values by other authors. Several views for the orbitals of NH_3[5-8] has been already reported, however we can not always compare those with the present results since those orbitals are almost described in

2) D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)*, **A193**, 299 (1948). This result for $2pz$ function can be approximated in the following analytical form:

$$(3/4\pi)^{1/2}\cos\theta_z r[1.809\,e^{-1.387r}+6.620\,e^{-2.950r}]$$

We calculated q_{pz} by this function.

3) G. R. Gunther-Mohr, R. L. White and A. L. Schawlow, *Phys. Rev.*, **94**, 1184 (1954).

4) For example, M. Kotani et al., "Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955).

5) A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 217 (1953).

6) J. Higuchi, *J. Chem. Phys.*, **24**, 535 (1956).

7) H. Kaplan, ibid., **26**, 1704 (1957).

8) A. B. F. Duncan, ibid., **27**, 423 (1957).

MO and not in Heitler-London type. When we dare to compare, they have some differences from ours as above mentioned. Here Duncan and Pople's orbitals[5] are determined in such a way as the parameters in orbitals are well fitted to the experimental value of the dipole moment of NH_3, and Higuchi's ones[6] are obtained following Roothaan's SCF procedure[9], in which all the electrons in molecule take part in setting up MO, so that the orbitals are considered more accurate than the present and Duncan and Pople's ones. Also, Syrkin et al.[10] have estimated the ionic character of the structure from the base of the additivity of bond moment. On the other hand, our estimations are made taking into consideration the nuclear quadrupole coupling constant besides the dipole moment. However these both estimates may be said to be equal substantially.

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9) C. C. J. Roothaan, *Revs. Modern Phys.*, **23**, 69 (1951).
10) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond", Butterworths Scientific Publications, London (1950), p. 208.
11) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York (1945), p. 439.

Two Crystalline Forms of DL-α-*Amino-n-butyric Acid*

By Masamichi Tsuboi, Yoichi Iitaka, Shigeko Suzuki and San-ichiro Mizushima

(Received March 19, 1959)

In the course of our infrared studies on amino acids, we have found that there are at least two crystalline modifications in DL-α-amino-*n*-butyric acid,—one of which corresponds to the form already known (hereafter designated as A-form), while the other is a new form (B-form).

A-form is obtained as tabular crystals from the saturated aqueous solution on cooling. While, B-form is obtained as fibrous crystals from the aqueous solution (not necessarily saturated) by adding ethanol. The two forms give different

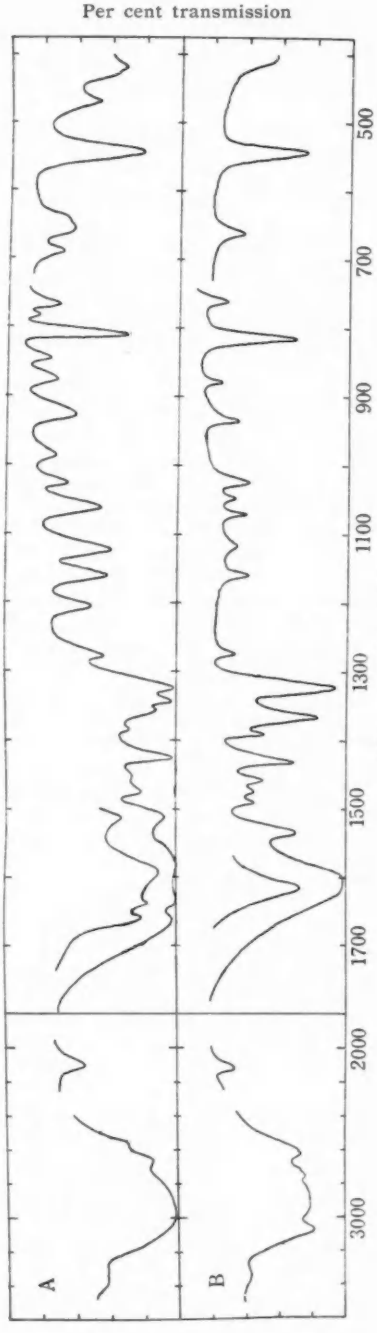

Fig. 1. Infrared absorption spectra of A- and B-forms of DL-α-amino-*n*-butyric acid.

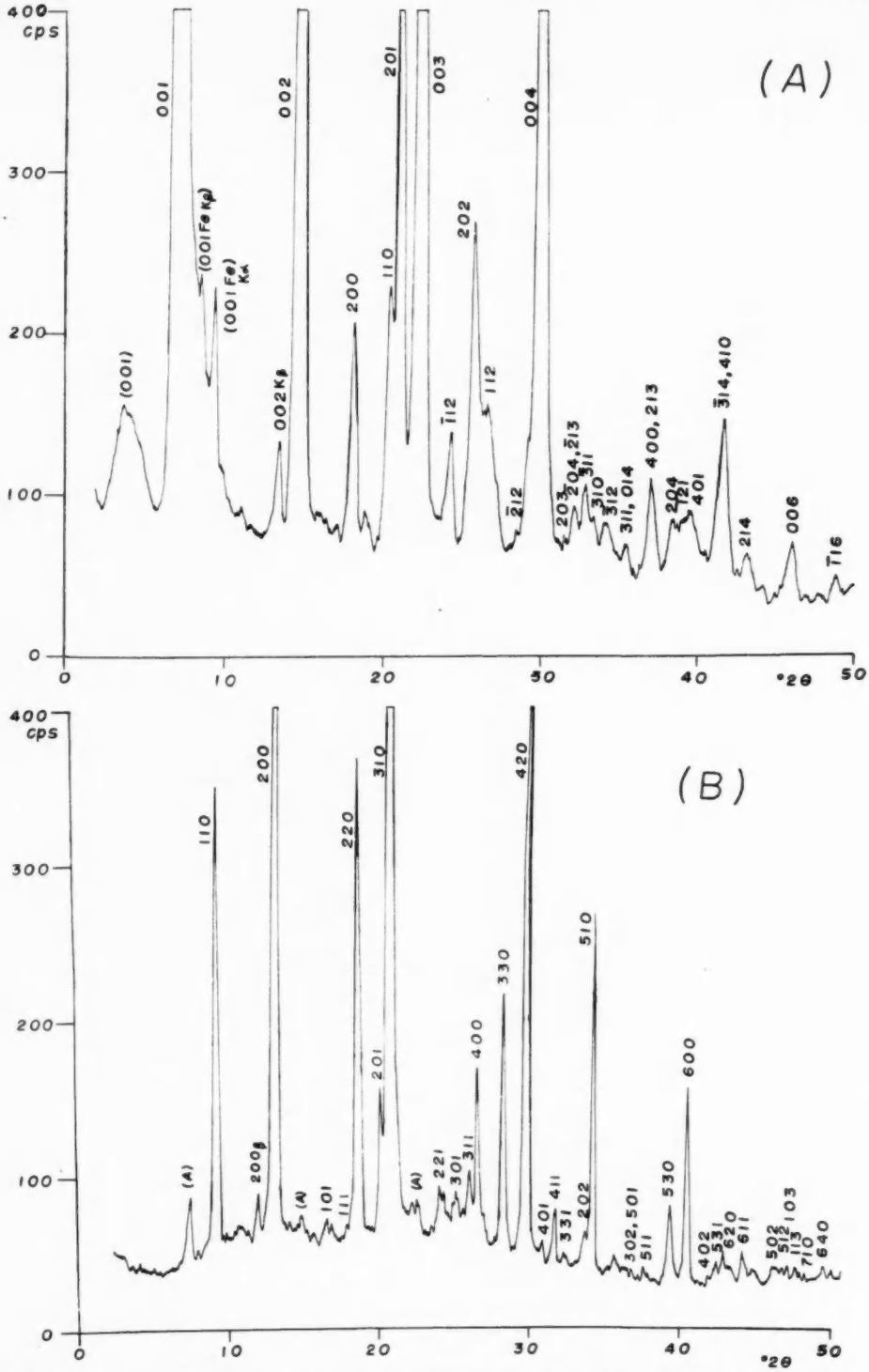

Fig. 2. X-ray powder patterns of A- and B-forms of DL-α-amino-n-butyric acid. Radiation used: Cu*K*, 30 kV., 15 mA., Ni-filtered. (The diffused peak indicated as (0 0 1) for A-form is the continuous spectrum of the X-ray diffracted by the (0 0 1) plane.)

infrared spectra and X-ray powder patterns as shown in Figs. 1 and 2. From the measurements at different temperatures it was found that B-form is transformed into A-form at 195°C, whereas A-form remains unchanged from room temperature to 200°C. Therefore, at room temperature B-form is stable and A-form is metastable, but above 195°C this form becomes stable.

By our X-ray and infrared investigations, A-form is identified as the one, for which Dawson and Mathieson[1] gave the following constants: $P2_1/a$, $a=9.87$ Å, $b=4.80$ Å, $c=12.10$ Å, $\beta=101°$, $Z=4$, and Koegel et al.[2] observed infrared spectrum.

For B-form, it was found, from oscillation and Weissenberg photographs about the axis of the elongation (c-axis) and the axis perpendicular to it (a-axis), that the crystal is tetragonal, with the Laue symmetry of $4/m$, and with the unit cell dimensions: $a=13.38$ Å, and $c=5.85$ Å. Analysis of the photographs showed systematic absence of the reflections for ($h\,k\,0$) planes when $h+k$ is odd, and for ($0\,0\,l$) planes when l is odd; indicating the space group of $P4_2/n$.

As to the molecular configurations of A- and B-forms, it was found probable, from our infrared measurements with plane polarized radiation, that the two forms are rotational isomers to each other[3]. Furhther analysis of the X-ray photographs is now in progress, from which it is hoped to determine accurately the configurations of these isomers.

We wish to thank Sister Mary Marina, for her sending us the infrared spectra of a crystalline DL-α-amino-n-butyric acid which now turned out to be A-form.

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1) B. Dawson and A. McL. Mathieson, *Acta Cryst.*, **4**, 475 (1951).
2) R. J. Koegel, R. A. McCallum, J. R. Greenstein, M. Winitz and S. M. Birnbaum, *Ann. N. Y. Acad. Sci.*, **69**, 94 (1957).
3) S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press, New York (1954).

A New Very Large Long-period in the X-ray Small-angle Diffraction of Polyethylene Filaments

By Takani MOCHIZUKI

(Received March 25, 1959)

The meridional long-period X-ray diffraction in polyethylene was measured by several authors[1-4]. However the reported long-period spacings are divergent. For instance, a spacing given by Kiessig[2] is 98 Å, whereas that by Statton[3] is 240 Å. These discrepancies might be due to the difference in polyethylene specimens and also their preparations.

This communication is to report that a further large long-period spacing has been observed recently in the meridional small-angle scattering for low-pressure polyethylene filaments.

Polyethylene ("Fortiflex A" of Celanese Corp. of America; Melt index: 0.7) filament specimens were prepared with an extruder at 210°C (Sample A), and stretched at 140°C up to 100% (Sample B), 200% (Sample C) and 300% (Sample D). From the X-ray diffraction photographs, a fairly high orientation of the crystallites was seen for Sample A and a typical uniaxial orientation of the crystallites was observed for Sample D. The small-angle scatterings of X-rays from these samples were

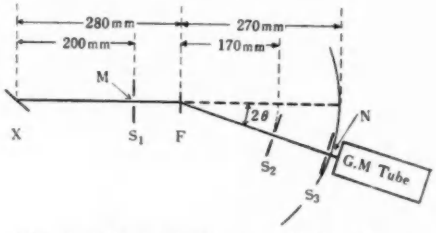

Fig. 1. Schematic diagram of the X-ray diffractometer.
X: X-ray focus
S_1: 1st slit 0.15 mm.
S_2: 2nd slit 0.5 mm.
S_3: 3rd slit 0.1 mm.
F: filament sample
M, N; Soller slit

1) E. P. H. Meibohm and A. F. Smith, *J. Polymer Sci.*, **7**, 449 (1951).
2) K. Hess and H. Kiessig, *Kolloid-Z.*, **130**, 10 (1953).
3) W. O. Statton, *J. Polymer Sci.*, **28**, 423 (1958).
4) I. Sakurada, Y. Nukushina and Y. Tanaka, *Chem. of High Polymers*, **15**, 771 (1958).

measured in the direction parallel to the fiber axis with an X-ray diffractometer having the following slit system, shown in Fig. 1, Cu $K\alpha$ radiation (38 KV. 15 mA) filtered with nickel foil being used.

Curves of the diffracted X-ray intensity are shown Fig. 2. All samples show a very strong and distinct peak of intensity. The center of the peak for Samples A and D is found using Bragg's law to correspond to a spacing of the order of 260 Å and 460 Å, respectively. Such a large long-period of about 460 Å has not been observed previously for synthetic polymers. From the intensity curves of Samples B and C, it seems that two kinds of long-period (260 Å and 460 Å) coexist in these samples.

Further, high-pressure polyethylene ("Tenite #864" of Eastman Chem. Products; Melt index: 0.3) was examined for comparision. Filaments were prepared in the same way as above, and stretched up to 270% at 100°C (Sample E). The intensity curve of the meridional small-angle interference of Sample E is given by the dotted line in Fig. 2, which shows a broad and low intensity peak. The Bragg distance of this peak is calculated to be 177 Å,

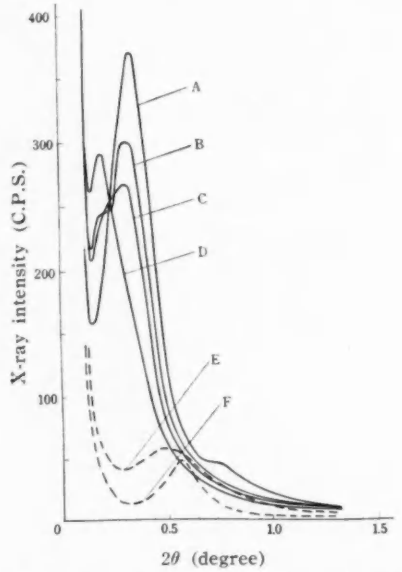

Fig. 2. Intensity curves of small-angle X-ray scattering.
A: original filament
B: 100% stretched filament
C: 200% stretched filament
D: 300% stretched filament
E: high-pressure polyethylene filament
F: polyvinyl alcohol fiber

which is in agreement with the value given by Meibohm and Smith[1] and Sakurada, Nukushina and Tanaka[4].

Some points of interest come to light in this experiment. In the low-pressure polyethylene, a very strong small-angle interference was observed as compared with the intensities obtained for high-pressure polyethylene and polyvinyl alcohol fibers[5]. It seems likely that this marked difference in the intensities might be partly due to the difference between the mean electron densities of the crystalline and amorphous parts, and has something to do with similar difference, shown in Fig. 3, in intensities of the meridional reflections (0 2 0) from both samples[5].

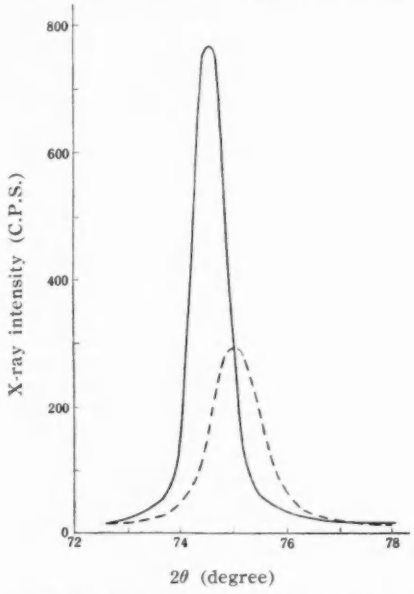

Fig. 3. Intensity curves of (0 2 0) reflection —— polyethylene ------ polyvinyl alcohol

Besides, it is to be noted that the curve A shows a second intensity hump. It corresponds to the second order reflection of the spacing of 260 Å. Such small intensity hump has not been observed in the curves B, C and D, and hence, it seems that the regular fine texture is destroyed by stretching process.

The author expresses his sincere thanks to Professor I. Nitta, Osaka Univercity, for his kind guidance and encouragement

5) The detailed results of polyvinyl alcohol fibers will be reported elsewhere.

throughout this experiments. He is also indebted to Mr. S. Miyazaki for supplying the samples.

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Isotopic Exchange of Zinc Chelate Compounds in an Anhydrous Organic Solvent

By Kazuo Saito and Michiko Tamura

(Received March 31, 1959)

Isotopic exchange of zinc in its complexes has been studied by a few workers with various chelate compounds[1-3]. It is generally agreed that the exchange is rapid, except that of zinc phthalocyanine complex, which has a "fused ring" structure. All these experiments, however, involve the use of water, either as solvent or as separating agent for the two compounds between which the isotopic exchange is to be examined. The present authors are of the opinion that the exchange might be accelerated by water, as is in the case of other metal complexes, and that, when the experiment is carried out in the absence of water, a measurably slow exchange might be expected even for those ions having filled inner *d*-orbitals.

Attempts have been extensively made to separate two chelate compounds of zinc in an anhydrous organic solvent. It was eventually found that pure zinc oxinate is precipitated, when dioxane solution of zinc oxinate and acetylacetonate is treated with a large excess of *iso*-propylether, trichloroethylene or chloroform. The yellow precipitate was spectrophotometrically examined in methanol and found to be free from acetylacetonate. The isotopic exchange was examined with inactive oxinate and acetylacetonate labelled with radioactive zinc-65. A linear relationship was observed, when the counting rate of the photo-multiplier pulse due to photo-electric peak of the γ-ray spectrum (1.114 MeV.) of zinc-65 is plotted against the amount of the labelled compound. In order to avoid the influence of water, all procedures were carried out in a dry box (relative humidity, less than 10%; dew point, below -14°C).

It was elucidated that the exchange proceeds instantaneously, even under an anhydrous condition. Since the exchange between zinc acetylacetonate in solution and solid zinc oxinate proceeds slowly, it appears evident that the rapid exchange took place in the homogeneous solution rather than between the solute and the precipitate in the nascent state.

Further work with other chelate compounds is in progress. Details of the study will be published later.

Experimental.—The chelate compounds were prepared by the usual methods and dried at 110°C immediately before use. The organic solvents were refluxed with sodium and distilled with dry apparatus. The presence of water was tested with various reagents, including anhydrous copper sulfate and cobalt chloride, but the results were all negative. It appears as if the water content is less than 0.01%.

Dioxane solution of zinc oxinate (0.000125

Table. Exchange of zinc between oxinate and acetylacetonate

No.	acetylacetonate used mg.	acetylacetonate c.p.m.	oxinate used mg.	oxinate recovered mg.	oxinate obsvd. c.p.m.	oxinate calcd.* c.p.m.	exchange %
1)	32.7	3277	44.2	29.0	1137	1075	106
2)	33.6	2208	44.3	41.7	1062	1039	102
3)	29.3	1966	44.2	40.4	77	1236	7
4)	32.9	2161	44.2	42.0	772	1026	75

1) 2): Both chelates in dioxane; time of exchange, 30 sec.
3) 4): Acetylacetonate, in the mixed solvent; oxinate, solid; time of exchange, 3) 1 hr., 4) 12 hr.
* Calculated on the assumption that a complete exchange has taken place.

1) Don C. Atkins, Jr. and C. S. Garner, *J. Am. Chem. Soc.*, **74**, 3527 (1952).
2) L. Leventhal and C. S. Garner, ibid., **71**, 371 (1949).
3) A. Turco, G. Sordillo and M. Scatena, *Ricerca Sci.*, **25**, 2361 (1955).

mol. in 15 ml.) and that of zinc acetylacetonate (0.000125 mol. in 25 ml.) were mixed (at room temperature, 18°C) and, after 30 sec., *iso*-propylether (ca. 300 ml.) was added. The precipitate was filtered off with a detachable sintered glass filter plate, thoroughly washed with *iso*-propylether, weighed and submitted to γ-ray counting. Precipitation of the oxinate was completed within one hour. (No. 1 and 2 in the table).

Exchange between solid oxinate and acetylacetonate in solution was examined in a mixture (100 ml.) of dioxane and *iso*-propylether (1+3, by volume). About 7 and 75 per cent exchange were observed after one hour and 12 hours, respectively. Since the mixed solvent assumed yellow, the exchange appears to proceed through partial dissolution of the oxinate.

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*Crystalline Polymers of Some Nuclear-substituted Styrenes**

By Shunsuke MURAHASHI, Shun'ichi NOZAKURA and Hiroyuki TADOKORO

(Received April 9, 1959)

In the preceding paper we pointed out the possible crystallization of poly(*p*-methylstyrene) and poly(*m*-methylstyrene) prepared by Ziegler's catalyst from the observation of infrared spectra and density-measurements[1]. In the present communication, we wish to report that this expectation has been realized by the suitable heat-treatment in both cases and also a newly prepared poly(*p*-trimethylsilylstyrene) has been found to crystallize easily by the same treatment.

These results stand in contrast with the recent observation by Natta that the polymers of *p*-substituted styrene obtained with Ziegler's catalysts are generally amorphous, except for *p*-fluorostyrene, because of a steric hindrance caused by the *p*-substituent in crystallization[2].

TABLE I. POLYMERIZATION OF NUCLEAR-SUBSTITUTED STYRENES WITH ZIEGLER'S CATALYST AT 70°C IN 20 ML. OF *n*-HEPTANE

Monomer g.	$TiCl_4$ mmol.	$AlEt_3$ mmol.	$AlEt_3$ added after washing mmol.	Time hr.	Conversion %	$[\eta]$[a]	Softening point °C[b]
p-Methylstyrene, 3.7 g.	2.2	2.3	2.5	3.6	43	2.61	130
m-Methylstyrene[c], 3.3 g.	3.2	3.4	3.4	3.5	21	2.52	90
p-Trimethylsilylstyrene[d], 4.3 g.	3.3	3.4	3.4	4.3	13	See Table II	

a) Intrinsic viscosity in toluene at 30°C.
b) Softening points were observed under a microscope.
c) *m*-Methylstyrene was supplied from the Research Laboratory of Dainihon Celluloid Co.
d) *p*-Trimethylsilylstyrene was supplied from the Engineering Laboratory of Mitsubishi Electric Manufacturing Co.

TABLE II. FRACTIONAL EXTRACTION OF THE CRUDE POLY(*p*-TRIMETHYLSILYLSTYRENE)[a]

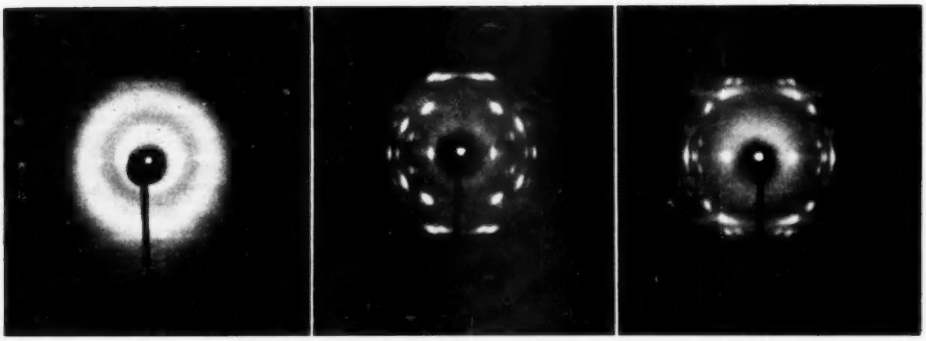
Solvent for extraction	Fraction %	$[\eta]$	Softening p. or m. p. °C[b]	X-ray evidence
Acetone	19	0.35	s. p. 125	Amorphous
Ether	11	0.61	s. p. 145	Partially crystalline
Benzene	70	2.49	m. p. 284	Highly crystalline

a) Hot extraction was carried out using a modified Soxhlet's extractor.
b) Softening points and melting points were observed under a polarized microscope.

* Paper III in a series on "Stereoregular Polymers".

1) H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhara and S. Murahashi, This Bulletin, **32**, 313 (1959).

2) G. Natta, F. Danusso and D. Sianesi, *Makromol. Chem.*, **28**, 253 (1958).



(a) (b) (c)

Fig. 1. Fiber diagrams of X-ray diffraction patterns.
(a) Poly(*p*-methylstyrene). An extruded filament was drawn at 135°C to about 20 times of the original length and heated for 6 hr. at the same temperature.
(b) Poly(*m*-methylstyrene). Drawn at 90°C to about 20 times and heated for 3 hr. at 100°C.
(c) Poly(*p*-trimethylsilylstyrene). Drawn at 150°C to about 20 times and heated for 0.5 hr. at 200°C.

All the polymerization procedure in this paper was performed by the use of Ziegler's catalysts according to the modified method described in the previous paper[3], i. e., the catalystic solid mass was washed with *n*-heptane prior to polymerization (Table I). The fractional extraction of the crude polymer was carried out in the case of poly(*p*-trimethylsilylstyrene) as shown in Table II.

The fiber diagrams of X-ray diffraction patterns with these polymers are shown in Fig. 1. Poly(*p*-methylstyrene) could be crystallized by the heat-treatment in a stretched state, although its crystallinity was rather low as shown in Fig. 1 (a). On the contrary, the benzene-fraction (Table II) of poly(*p*-trimethylsilylstyrene) was found to be crystallized easily and highly crystalline even in an unoriented state. Poly(*m*-methylstyrene) was more reluctant to crystallize than poly(*p*-trimethylsilylstyrene) in an unoriented sample.

Fiber periods observed are 12.9, 57.0 and 60.4 Å for the polymers of *p*-methyl-, *m*-methyl- and *p*-trimethylsilyl-styrene, respectively. The large values of identity periods of these polymers suggest some complicated nature of the helical structures of these isotactic polymers. The detailed X-ray analysis will be published elsewhere by Nitta and others.

These three polymers are all considered to be isotactic and to have the helical structure of trans-gauche alternate sequence from the inspection of the following infrared data. (1) The 2849 cm^{-1} CH_2 symmetric stretching band has almost no dichroism (or rather weak parallel dichroism), though the 2924 cm^{-1} CH_2 antisymmetric stretching band shows distinguished perpendicular nature, as is in the case of isotactic polystyrene[4]. This dichroic behavior indicates such an inclination of the triangle of the methylene group that the direction of H—H is nearly perpendicular to the fiber axis and the angle between the bisector of the angle H—C—H and the fiber axis is about 54°44′. (2) The four bands in the region of 1400~1100 cm^{-1}, which are considered to be closely associated with the helical structure in the previous paper[1], are also found in the polarized spectra of these three polymers, showing the same dichroic natures as the corresponding bands of the oriented isotactic polystyrene: 1364 (⊥), 1314 (⊥), 1297 (∥) and 1185 cm^{-1} (∥).

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3) S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, to be published in this Bulletin.

4) H. Tadokoro, N. Nishiyama, S. Nozakura and S. Murahashi, *J. Polymer Sci.*, in press.

*Organic Spot Tests. I. Detection of Acidic Compounds**

By Yujiro NOMURA

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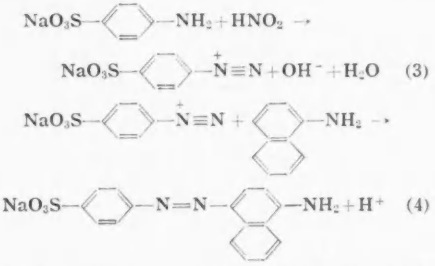
The familiar and sensitive Griess test for nitrites has been found to be used conversely for the detection of very small quantities of acidic compounds. Thus, the mixed solution of sodium sulfanilate, sodium nitrite and α-naphthylamine in dilute alcohol or dioxan produces intense red color on adding a tiny quantity of various acidic compounds. This color reaction depends on the formation of the red azo dye through the following successive reactions:

$$HA \rightleftarrows H^+ + A^- \quad (1)$$

$$NaNO_2 + H^+ \rightleftarrows HNO_2 + Na^+ \quad (2)$$



(3)

(4)

The reactions 3 and 4 proceed so rapidly and completely that the equilibria 2 and 1 are shifted toward the right successively. Accordingly, by virtue of the equilibrium disturbance it is possible to detect many organic acids which are not very soluble and are so weak that they do not affect usual dyestuff indicators at all or do indecisively at most.

Reagents.—1) 2.9 g. of sodium sulfanilate $NH_2C_6H_4SO_3Na \cdot 2H_2O$ and 0.7 g. of sodium nitrite are dissolved in 30 cc. of distilled water.

2) 1.8 g. of α-naphthylamine is dissolved in 40 cc. of ethanol or dioxane.

The reagent solution is prepared by mixing two solutions 1) and 2) just prior to use.

Procedure.—A few drops of the reagent solution are placed in a depression of a spot plate. A small amount of the test material (a few crystals or the residue after evaporating a drop of a test solution) is added. Depending on the acidity and solubility of the acid present, a red or orange color appears at once or after a few minutes. A comparison blank test is advisable when dealing with a slight amount of the sample.

Results.—The limits of detection attained with various acids were 25~40 γ. The following compounds were tested.

Immediate intense red color reaction.—Formic acid, acetic acid, propionic acid, butyric acid, isovaleric acid, caproic acid, oxalic acid, malonic acid, succinic acid, adipic acid, fumaric acid, maleic acid, lactic acid, thioglycolic acid, malic acid, citric acid, tartaric acid, benzoic acid, salicylic acid, anthranilic acid, sulfanilic acid, benzenearsonic acid, hippuric acid and picric acid.

Immediate orange to orange-red color reaction.—Caprylic acid, pelargonic acid, capric acid, palmitic acid, stearic acid, oleic acid, elaidic acid, erucic acid, cholic acid, aspartic acid and glutamic acid.

Orange color reaction within a few minutes.—Lauric acid, myristic acid and 12-hydroxyoleic acid.

Negative reaction.—Phenol, cresol, catechol, resorcinol, hydroquinone, ethyl acetate, ethyl benzoate, diethyl malonate, benzoylacetone, ethyl acetoacetate, acetanilide, succinimide and ammonium salts or metal salts of carboxylic and sulfonic acids.

α-Amino acids except aspartic acid and glutamic acid gave no response to the reagent solution. But after digesting with two or three drops of formaline they showed positive reactions. The following amino acids could be detected in this manner: glycine, alanine, cystine, valine, methionine, leucine, isoleucine, phenylalanine, tyrosine, histidine and asparagine.

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